1. ELI-ALPS
2. ULTRAFAST DYNAMICS GROUP
3. Development of step scan FTVIS experimental methodology @ ELI-ALPS to explore photoinduced chemical reactions in intense terahertz fields

Viktor Chikan, PhD
Kansas State University, Chemistry

Extreme Light Infrastructure Attosecond Light Pulse Source (ELI-ALPS)

Fulbright Distinguished Scholar Award

John von Neumann Distinguished Award in STEM

HUNGARY
Europe and Eurasia

twentieth-century Hungarian mathematician who made great contributions to quantum physics, functional analysis, mathematical set theory, communication sciences, economics, numerical analysis, cybernetics, the hydrodynamics of expressions and statistics.

He participated in the development of two of the first computers: ENIAC (Electronic Numerical Integrator And Computer) and EDVAC (Electronic Discrete Variable Automatic Computer). This is due to their interest in creating automation machines that would allow the automation of complex systems.

Extreme Light Infrastructure Attosecond Light Pulse Source (ELI-ALPS)

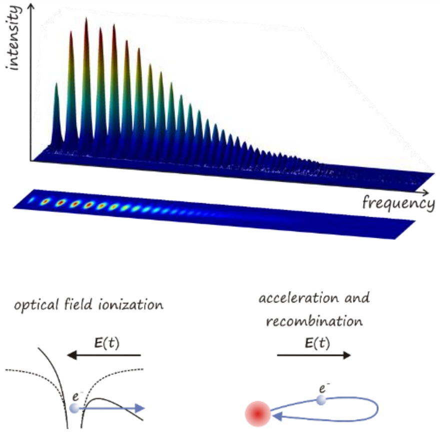
ELI- first civilian large-scale high-power laser research facility

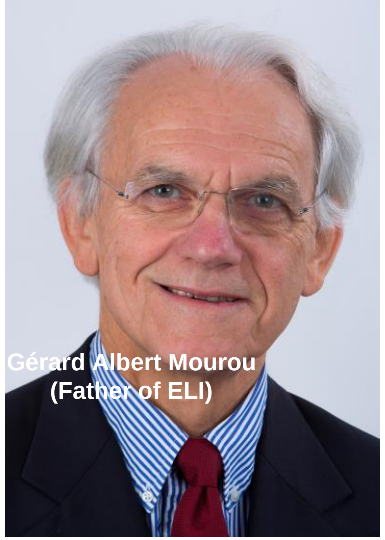
Colleagues@ ELI-ALPS

Goals:

To generate X-UV and X-ray femtosecond and attosecond pulses, for temporal investigation at the attosecond scale of electron dynamics in atoms, molecules, plasmas and solids.

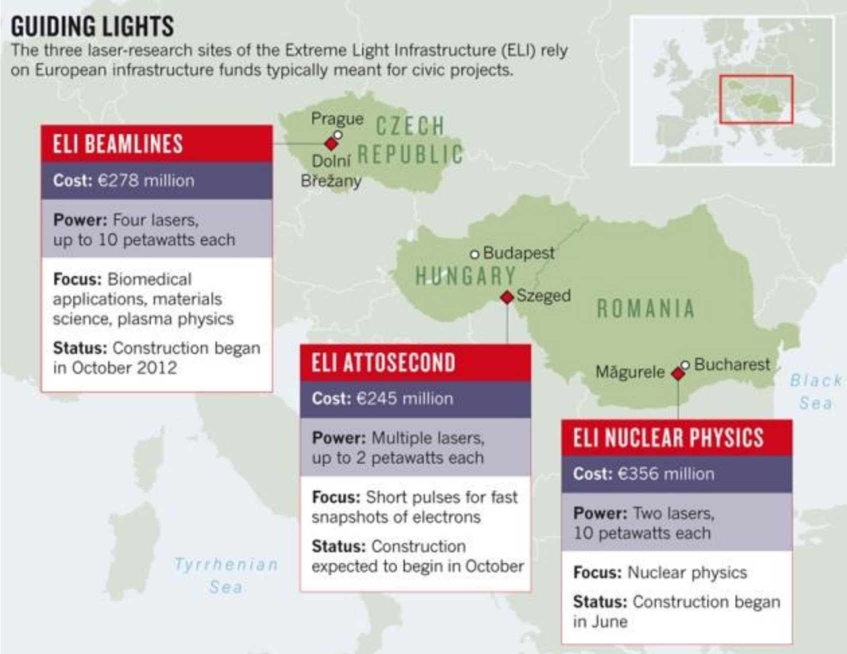
To contribute to the technological development towards high average power, high peak intensity lasers.

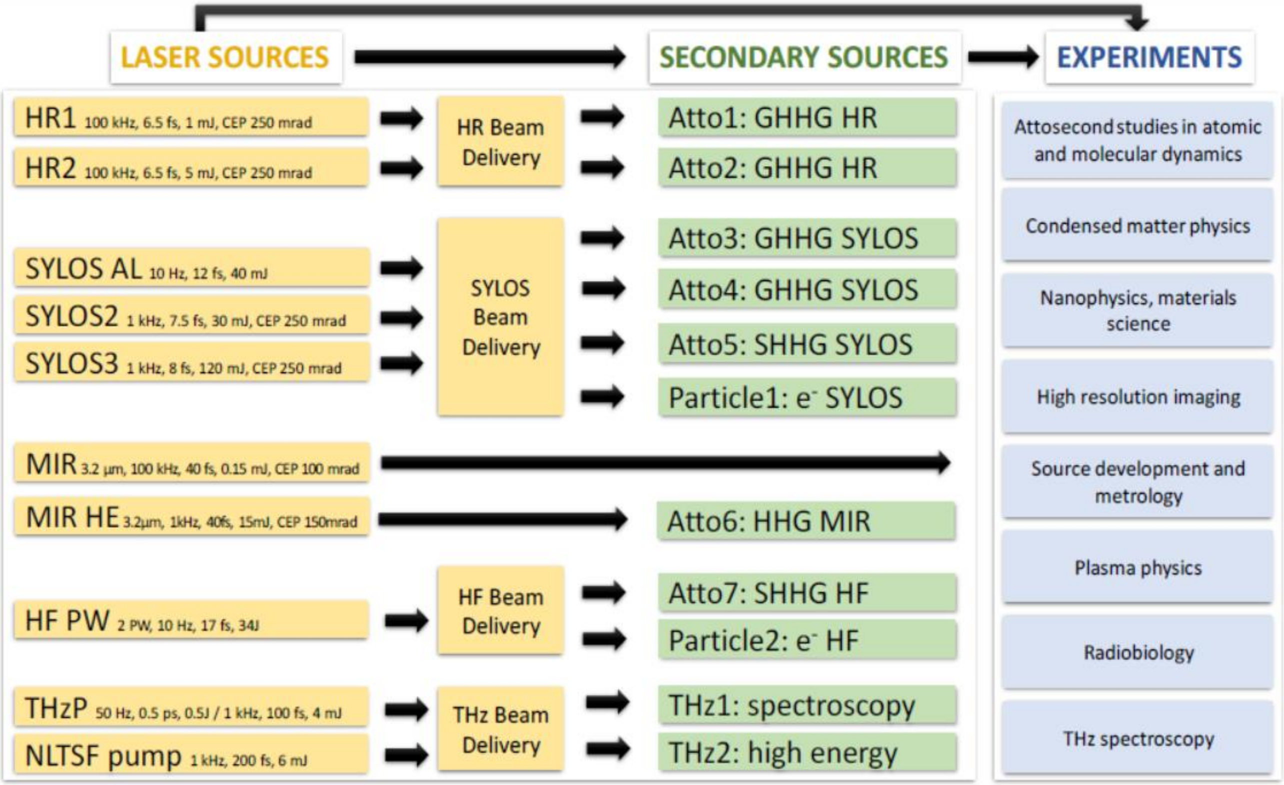


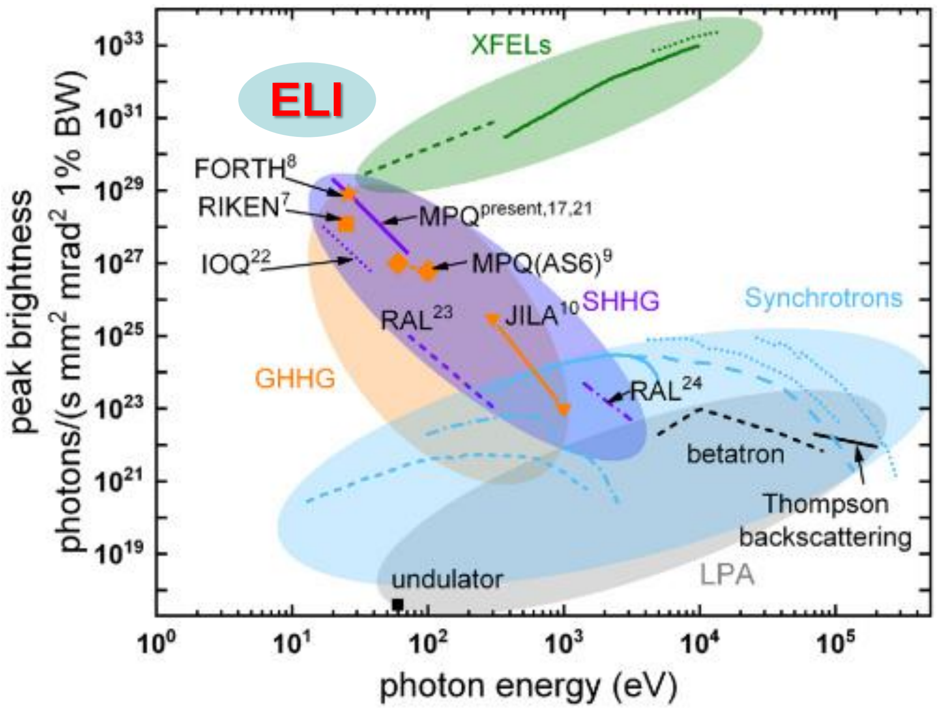


Gérard Albert Mourou
(Father of ELI)

ULTRAFAST DYNAMICS GROUP

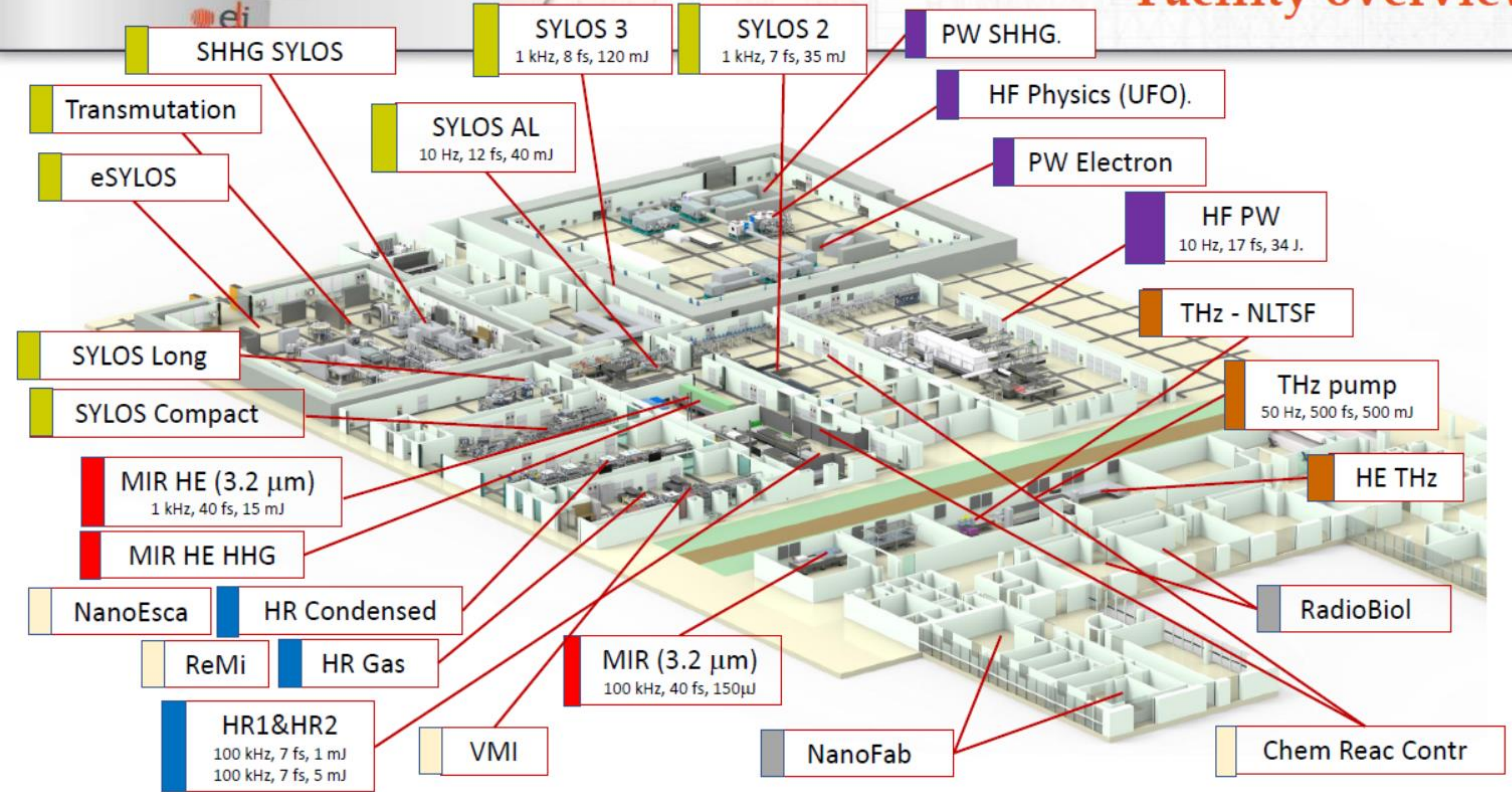






Olga Jahn, Vyacheslav E. Leshchenko, Paraskevas Tzallas, Alexander Kessel, Mathias Krüger, Andreas Münzer, Sergei A. Trushin, George D. Tsakiris, Subhendu Kahaly, Dmitrii Kormin, Laszlo Veisz, Vladimir Pervak, Ferenc Krausz, Zsuzsanna Major, and Stefan Karsch, "Towards intense isolated attosecond pulses from relativistic surface high harmonics," Optica 6, 280-287 (2019)

Facility overview

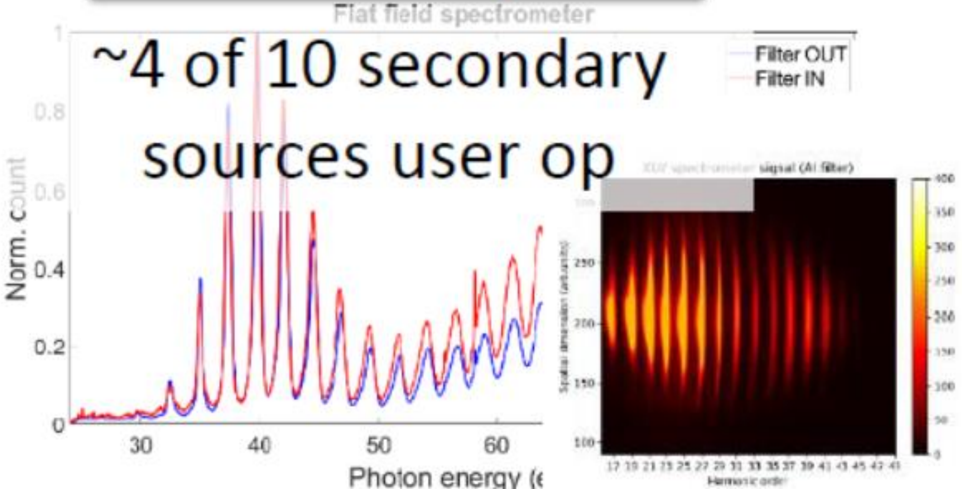


ELI ALPS - Achievements to date

Laser systems commissioned

5 of 9 lasers
user operational

1st attosecond pulses



~4 of 10 secondary
sources user op

Experimental stations / labs

5 of 12 experimental
stations
user operational

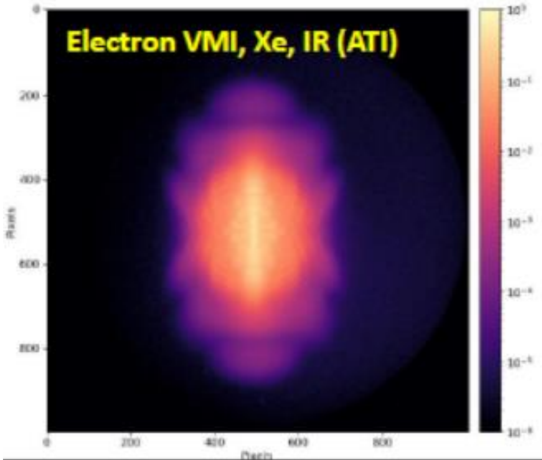
~40 completed
collaborative / user
campaigns
3000+ user hours

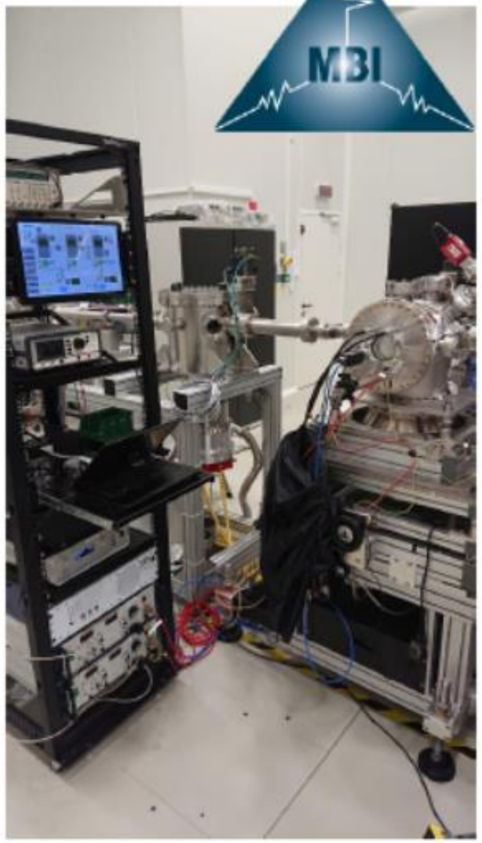
Experimental stations for gas phase studies

user ready
mobile stations

VMI-ES

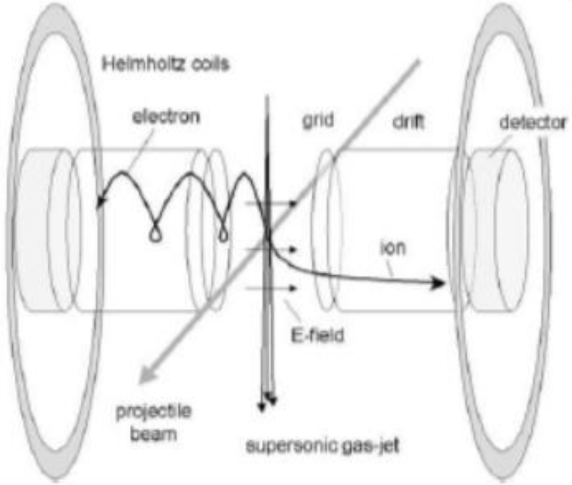
to obtain energy- and angle resolved information on ions and electrons resulting from the photoionization or photofragmentation of atoms, molecules or nanoparticles

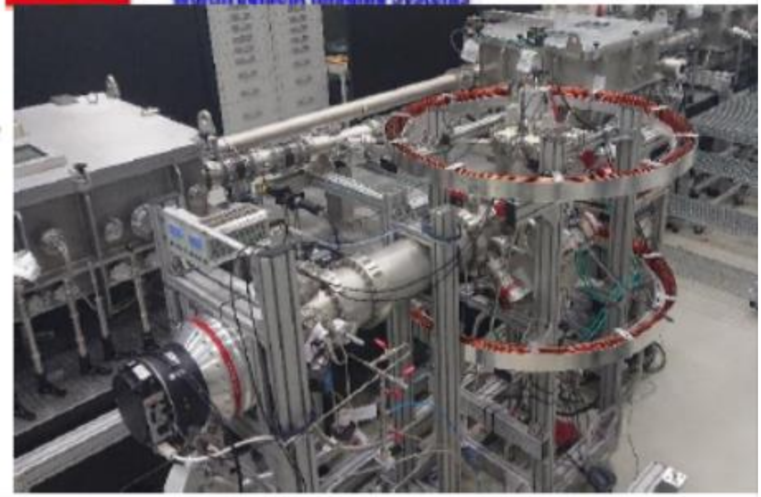




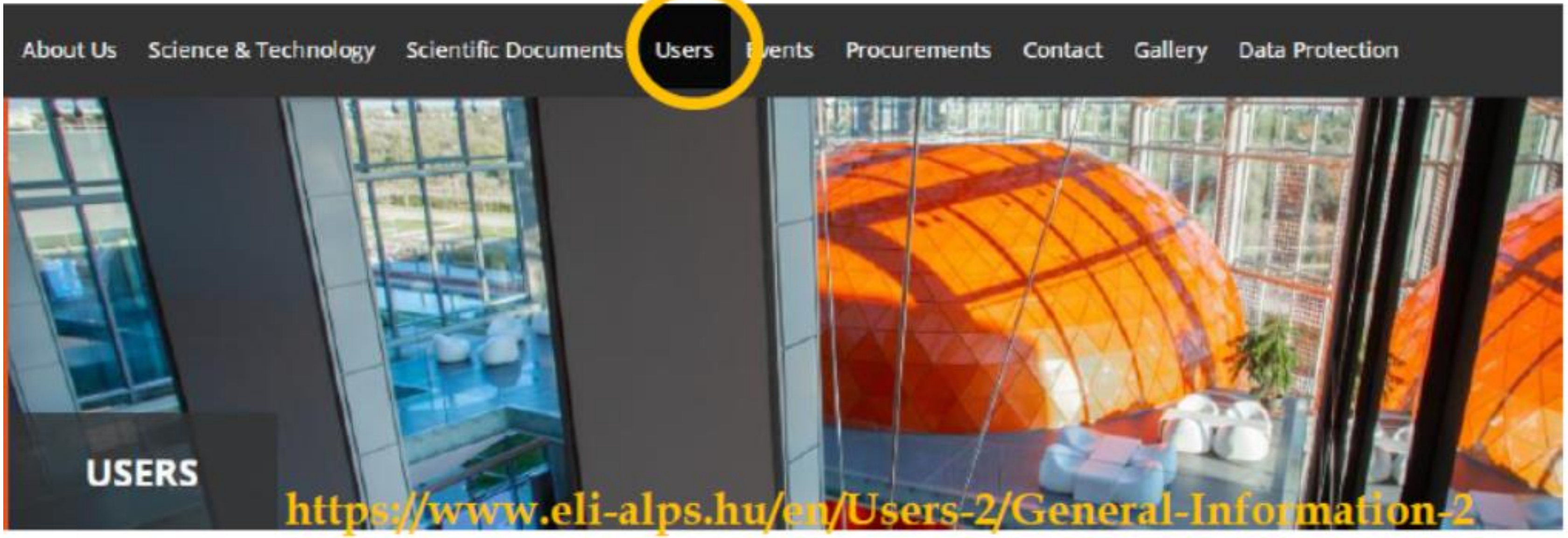
ReMi / Coltrims

Kinematically complete experimental study of ion and electron fragments detected in coincidence





ELI-ALPS User Call & Research Technology Information

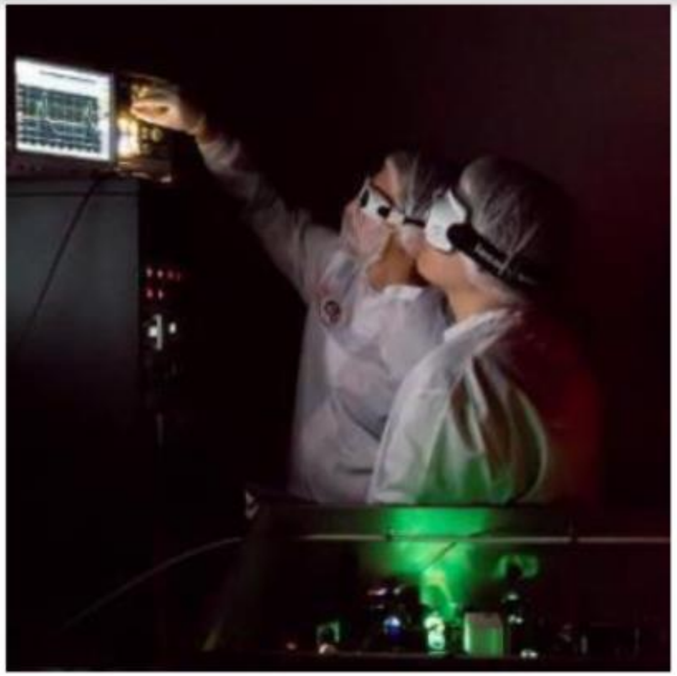


For information on our open user call, and details of our research technology infrastructure please visit our website.

user.office@eli-alps.hu

- Online proposal submission system
- ELI-ALPS provides beamtime as well as technical and scientific support for the experiments
- All proposals are evaluated through a peer review procedure, access is granted based on scientific excellence
- Travel grant for young researchers
- User office assists in project management, logistics arrangements, trainings, access procedures

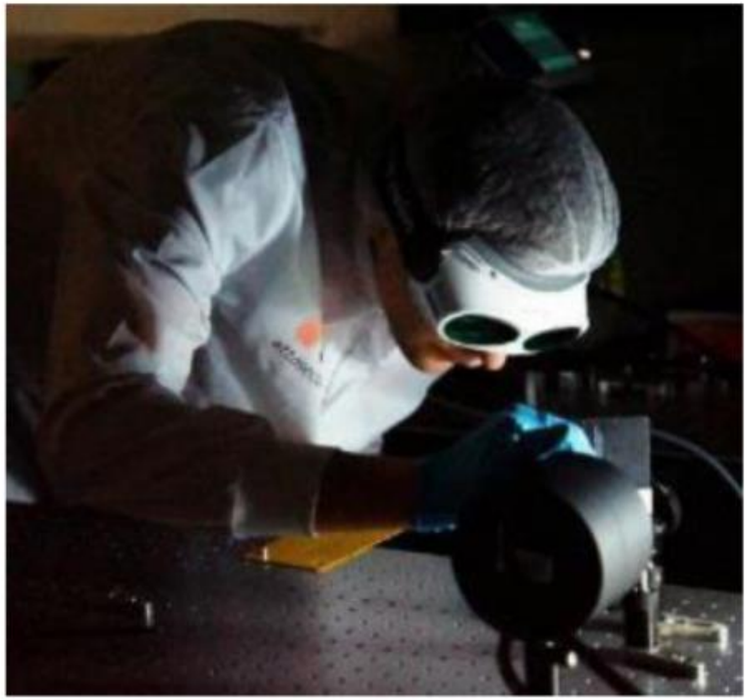
Virtual tour of ELI ALPS III. people



Open positions in

Laser science, AMO, condensed matter and plasma physics

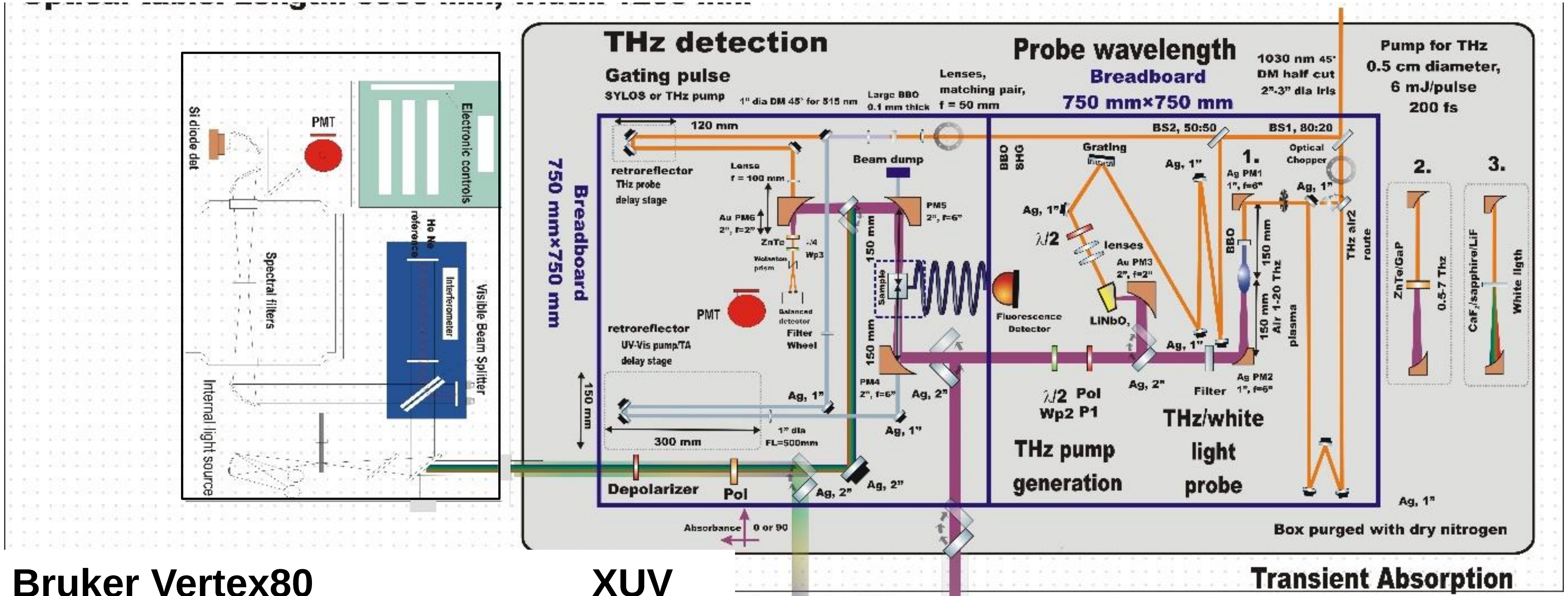
@ junior, postdoc and technician level



TRC setup – THz and LTA1 labs

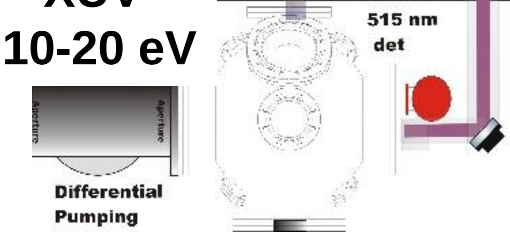
HR1 laser, 1 kHz, 100 mJ, 5 fs, 800 nm

Bandgap modulation, photodissociation (XUV attosecond –THz) and transient absorption experiments



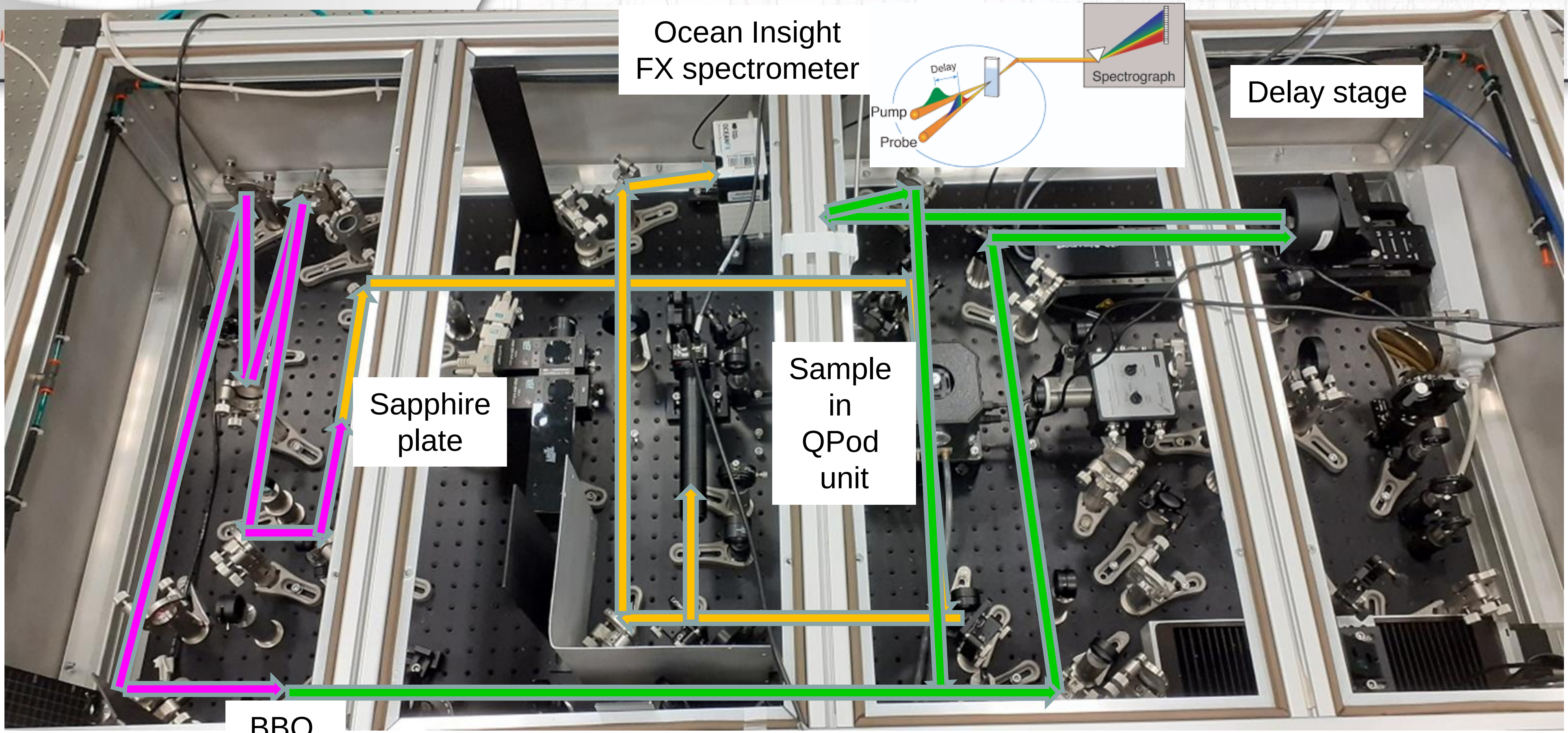
Bruker Vertex80
Fourier-transform spectromete
(200 nm-17 μm)
0.01 cm^{-1} spectral resolution
2.5 ns temporal resolution

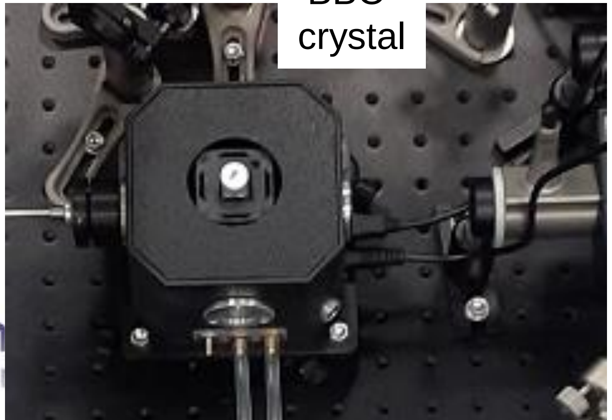
XUV
10-20 eV

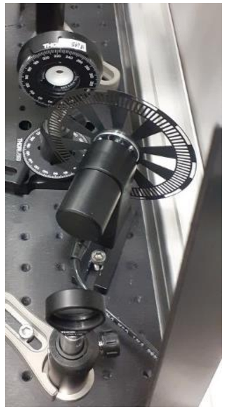


Pump and probe experiments:
Vis and THz pump
Vis,THz and fluorescence probe
temporal resolution: fs-ps

Transient absorption measurements with the HR-1 laser

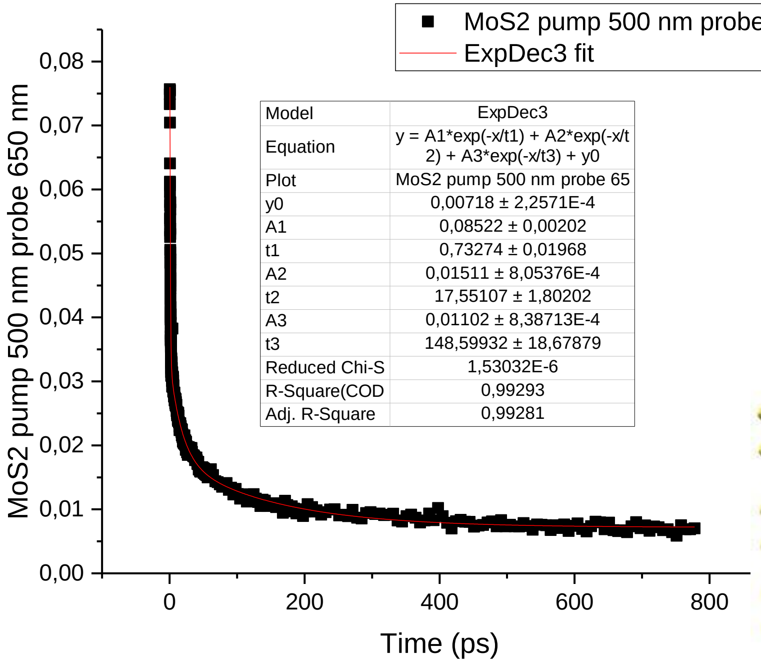




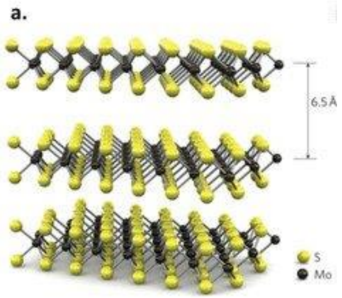


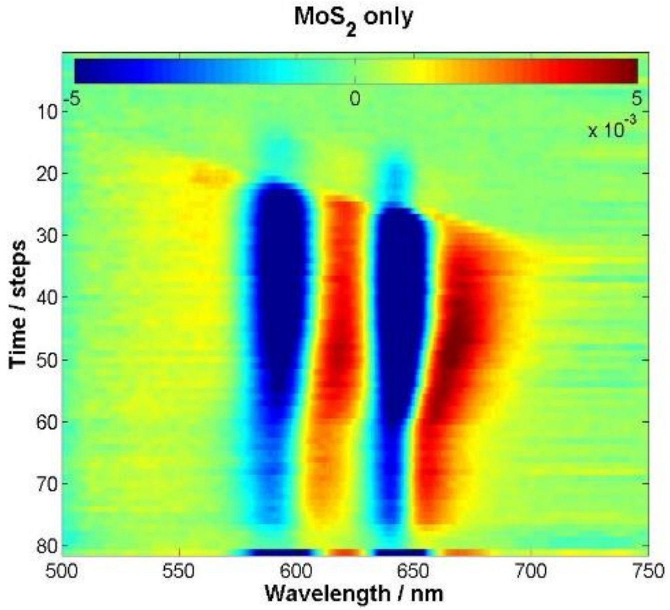
White light (probe beam) generation with sapphire plate (510-800 nm, FGB37 or FES0800 filters)
Green light (pump beam, SH) generation with BBO crystal (~100 fs, 100 kHz, FB500-40 filter, 480-520 nm)
Optical chopper used at 6 kHz for Lock-in measurements and 2 kHz for measuring the spectra

Validation experiments with MoS_2 film (reflection mode)



τ_1 = 732 fs
τ_2 = 17.6 ps
τ_3 = 148.6 ps





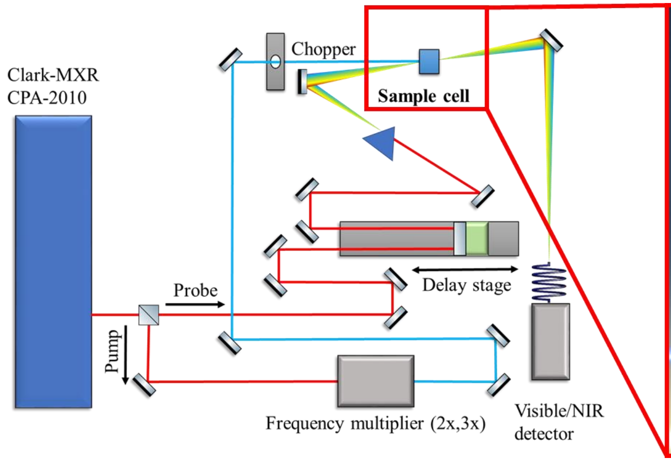
Nano Letters — Letter

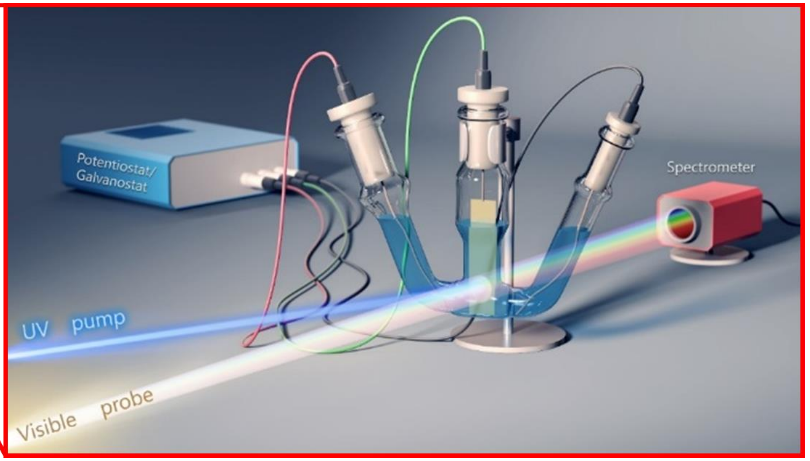
Table 1. Time Constants for the Decay of the B-Exciton (Monitored at 612 nm) within MoS_2-Only and MoS_2-Pentacene Heterojunction Films, after Excitation at 535 nm[a]

	τ_1 (A_1) carrier trapping	τ_2 (A_2) h^+ transfer	τ_3 (A_3) exciton–phonon scattering	τ_4 (A_4) radiative recombination and e^- trapping	τ_5 (A_5) charge recombination
MoS_2-only film	670 ± 20 fs (0.47)		15.8 ± 0.6 ps (0.35)	431 ± 20 ps (0.18)	
MoS_2–pentacene junction	670 fs[b] (0.48)	6.65 ± 0.34 ps (0.28)		431 ps[b] (0.09)	5.13 ± 0.44 ns (0.15)

Nano Lett. 2017, 17, 1, 164–169

Transient Spectroelectrochemistry





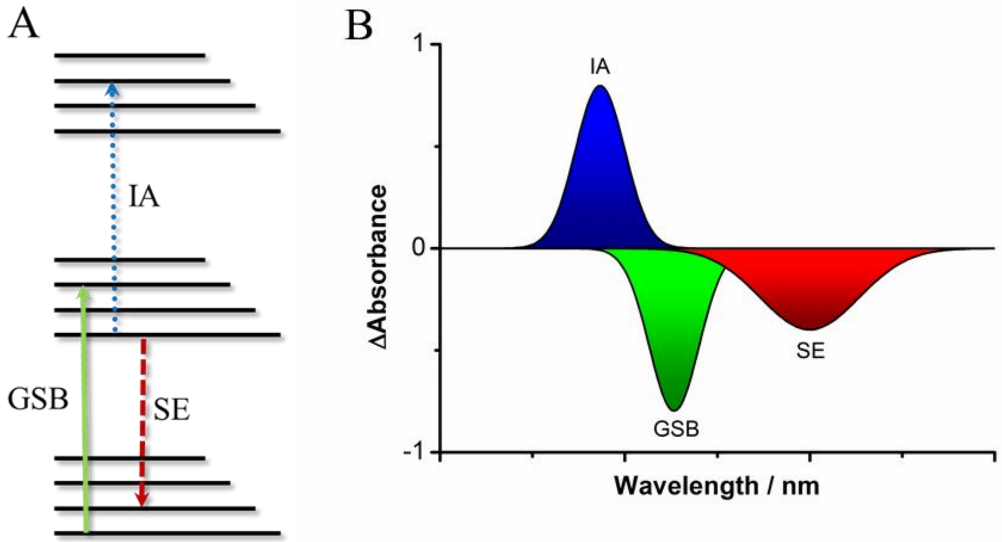
Two pulses of light interacts with the sample:

- Pump pulse (variable wavelength)
- Probe pulse (white light continuum)

Chopper to record spectra before and after pump pulse – **Difference spectra**

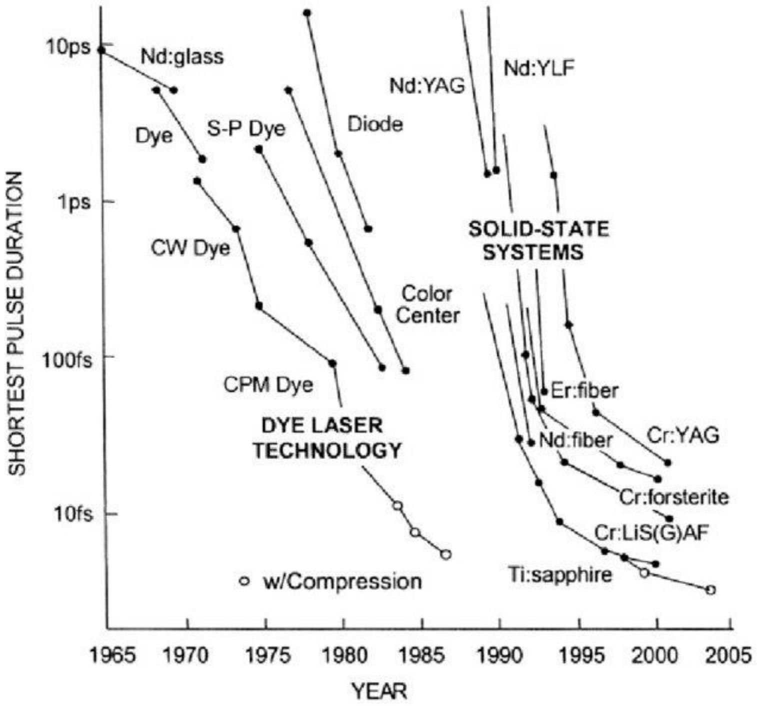
Delay stage induces a variable time difference between the pump and the probe pulse

Apply electrochemical bias and observe its effect on charge carrier recombination dynamics

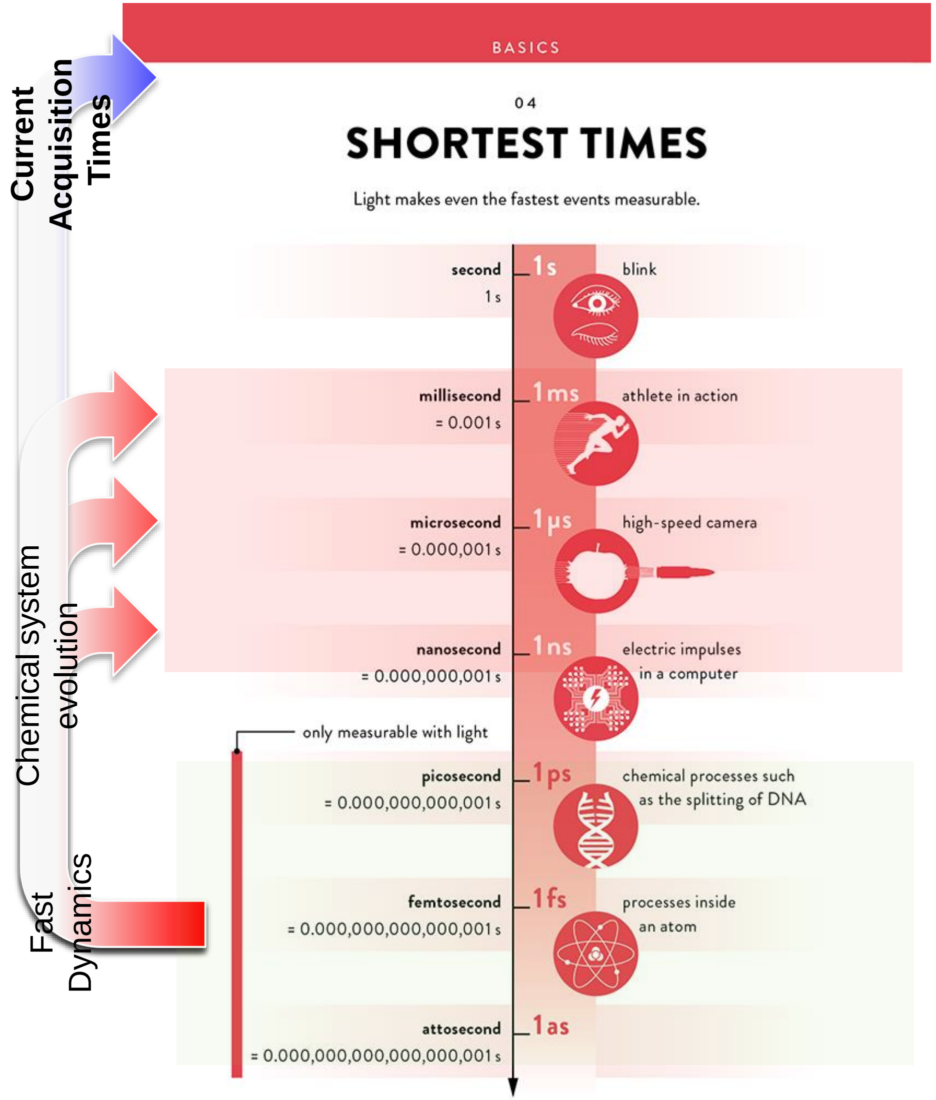


Kärtner, F. X.; Ippen, E. P.; Cundiff, S. T., Femtosecond Laser Development. In *Femtosecond Optical Frequency Comb: Principle, Operation, and Applications*, Ye, J.; Cundiff, S. T., Eds. Springer US: Boston, MA, 2005; pp 54-77.

Motivation



- Transient absorption/Flash photolysis(1950 by George Porter and Ronald G. W. Norrish, Nobel prize in 1967 for extremely fast chemical reactions) is a pump-probe laboratory technique, in which a sample is first excited by a strong pulse of light from a pulsed laser of nanosecond, picosecond, or femtosecond pulse width or by another short-pulse light source such as a flash lamp.



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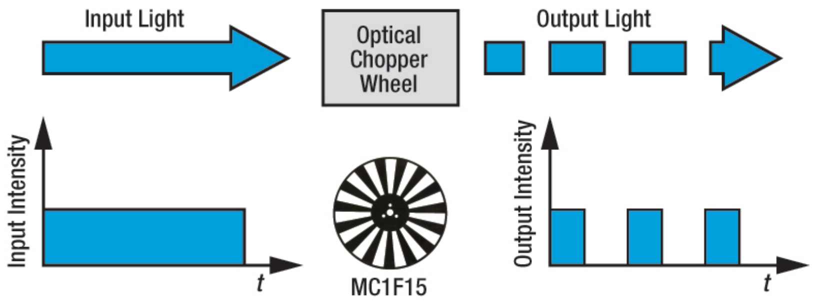
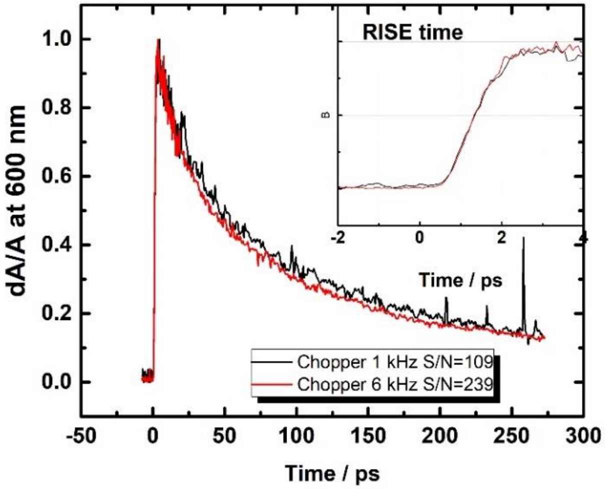
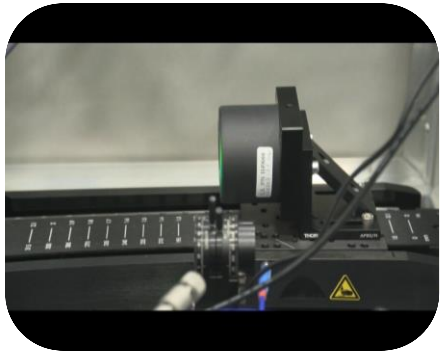
Reducing acquisition time → Fast detection

Single beam with chopper (lock in detection)

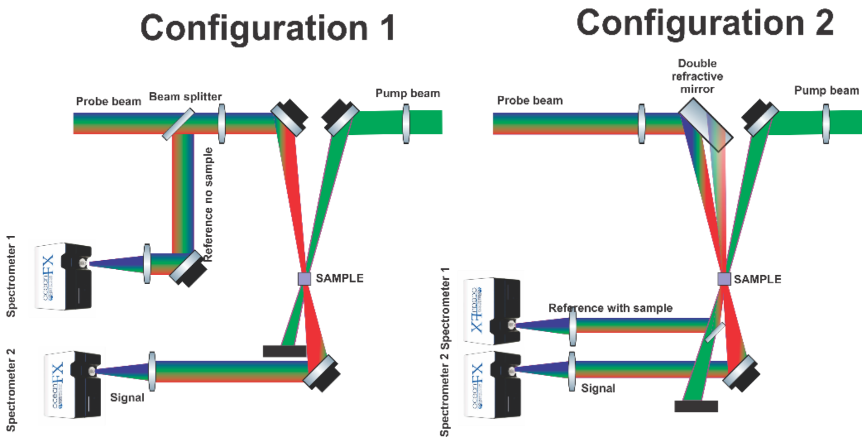


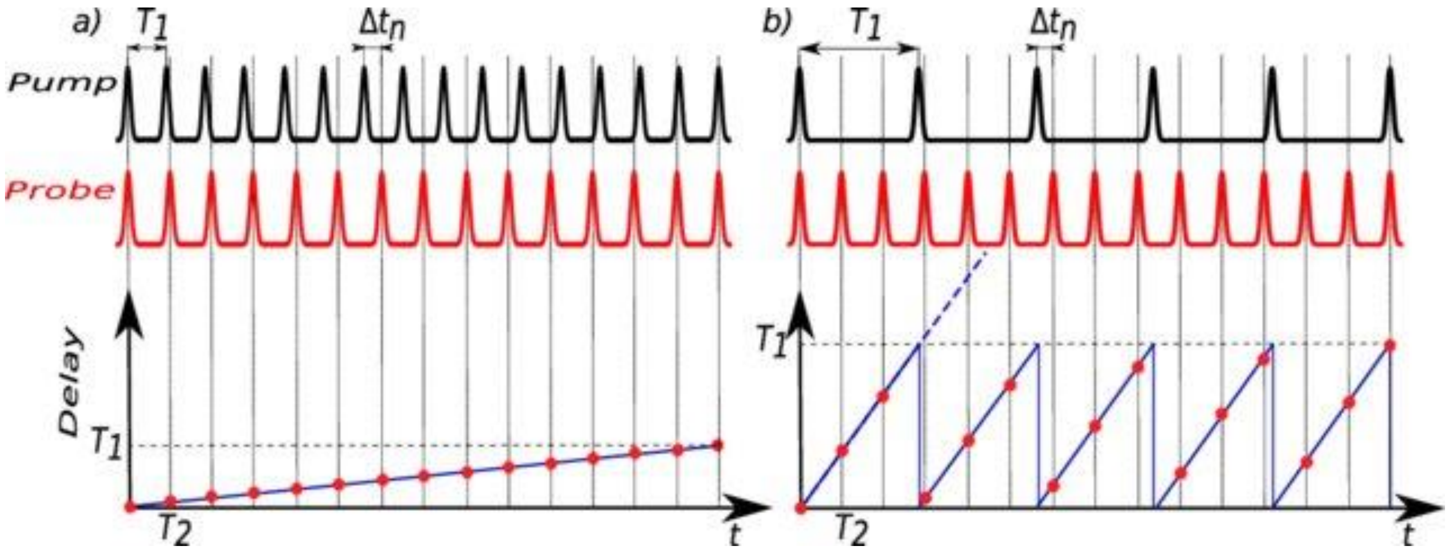
4,500 scans,
10 μs.
50000
buffer





Double Beam spectrometer





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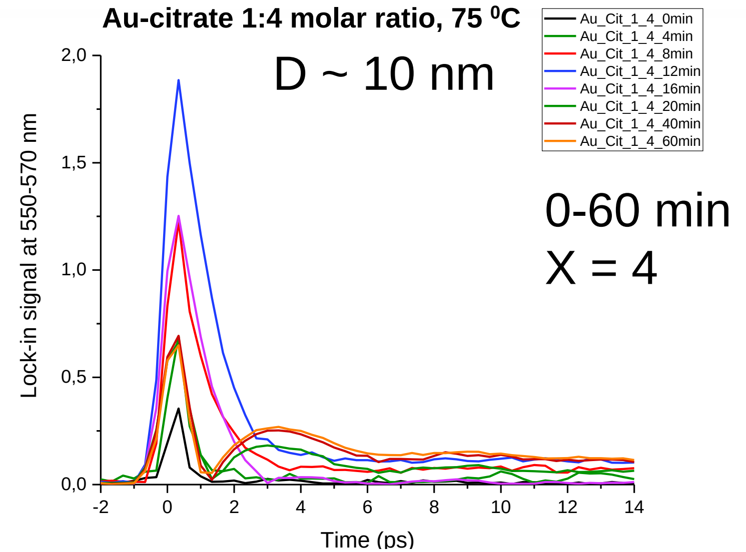
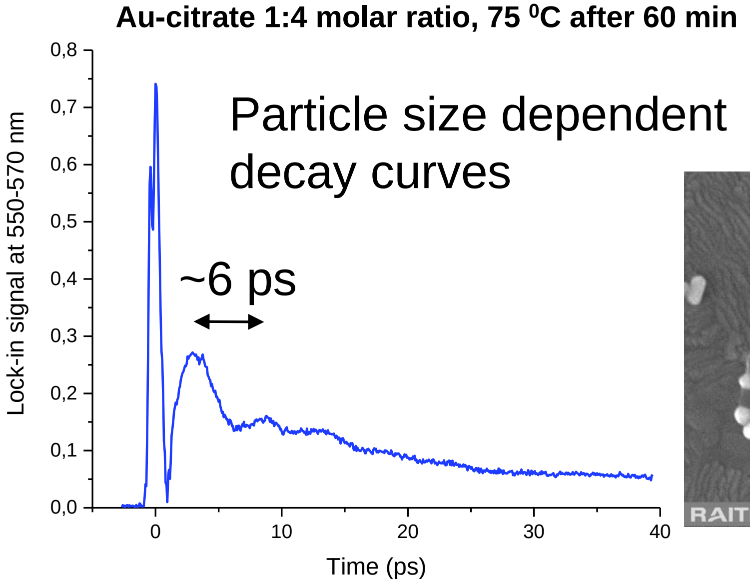
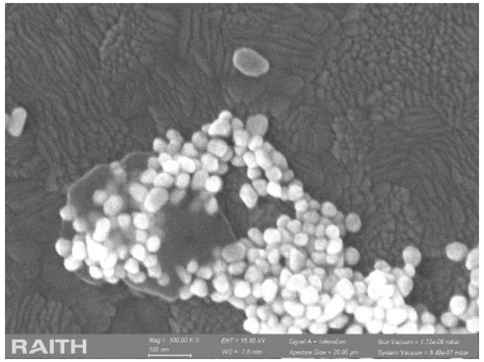
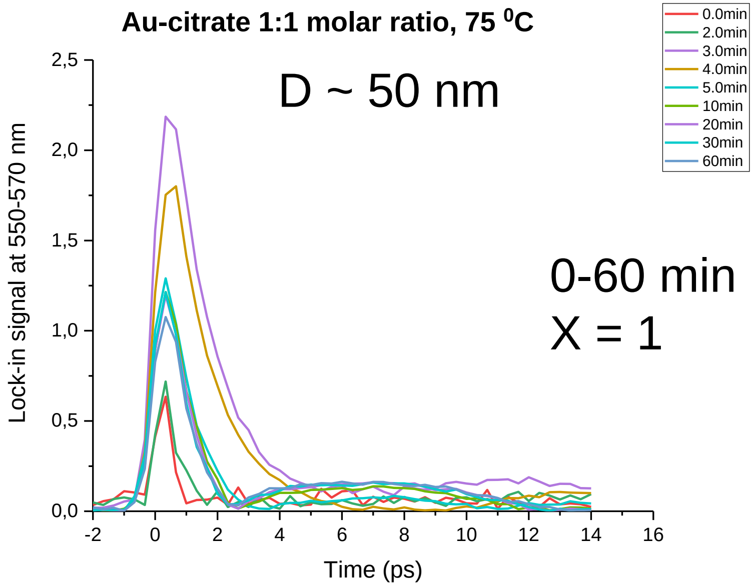
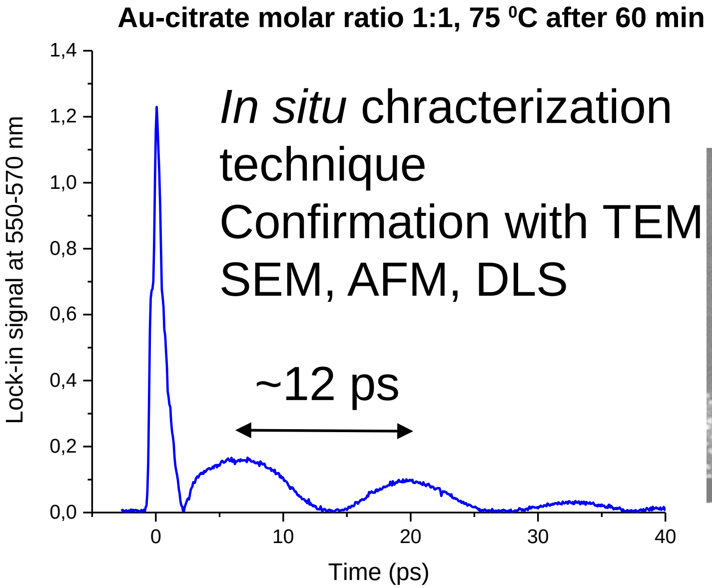
Laser induced acoustic vibrations of *in situ* synthesized gold NPs – particle size dependence Lock-in detection

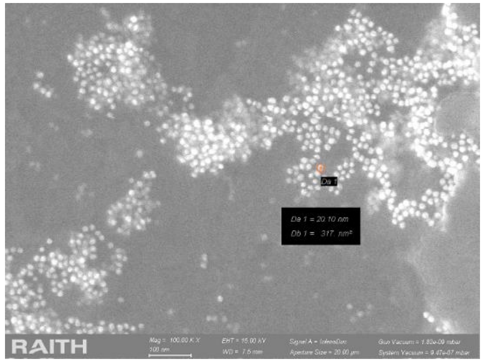




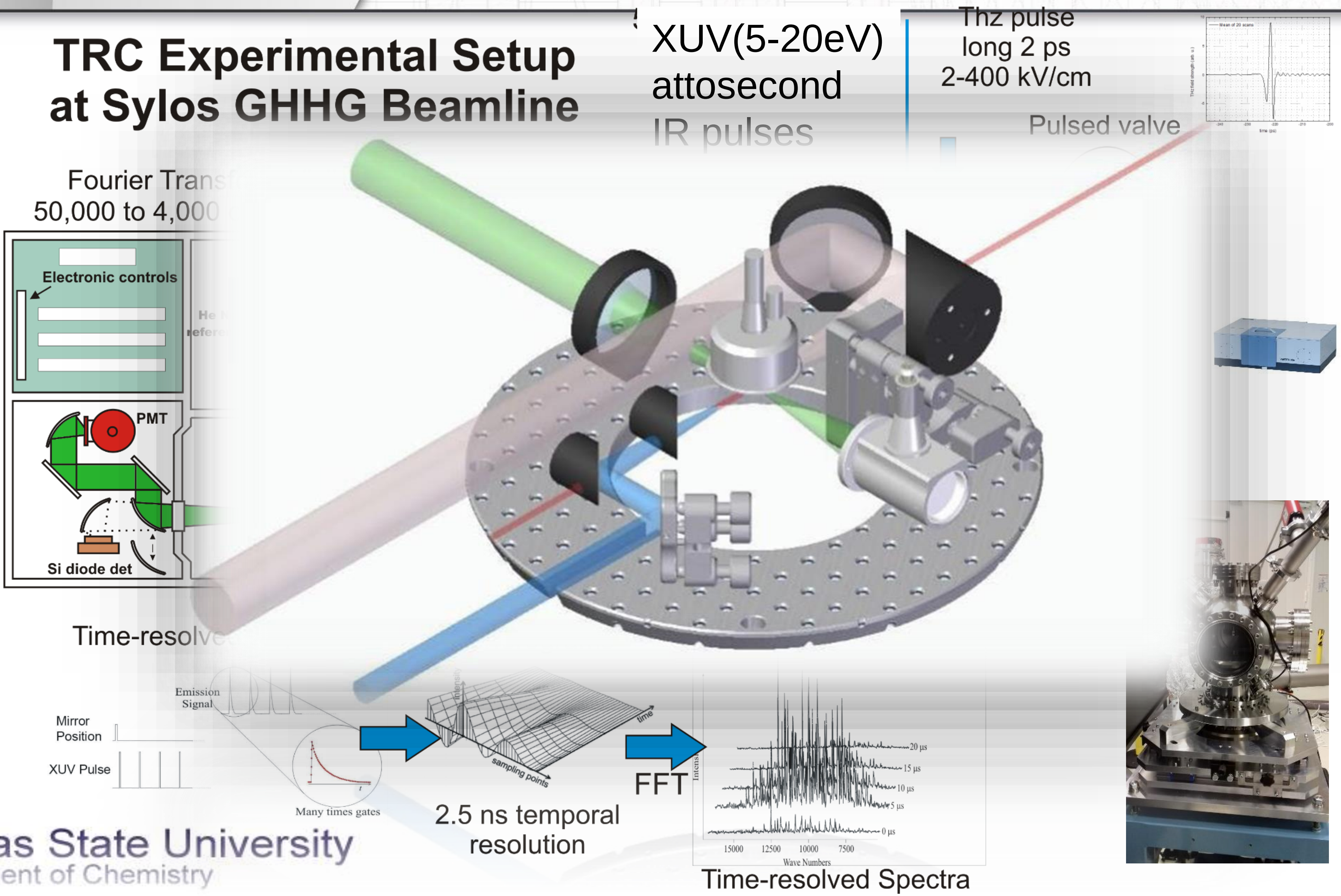








Detection: Experimental Arrangement



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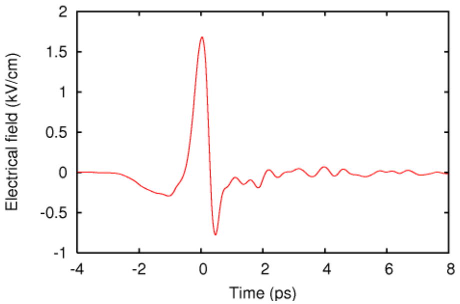
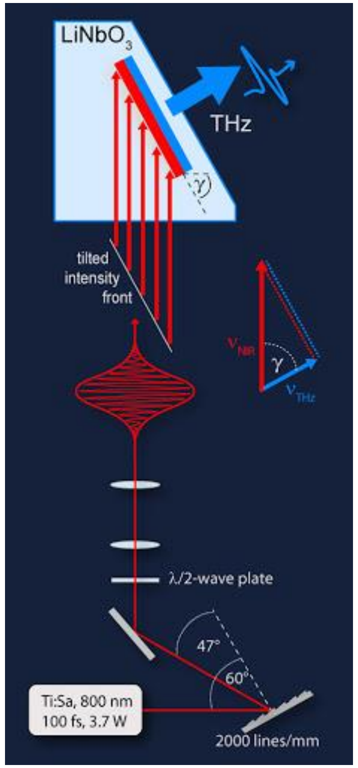
Long term Goal: Application of Terahertz Pulses



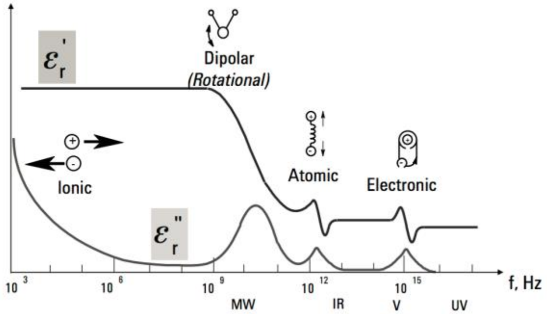
A) The role of amplitude of THz pulses

- **THz probe spectroscopy E_{max}≈ 100 V/cm |10 fJ investigating static and transient properties of materials Our recent work:** Optics Communications 2019, 436, 222-226. and JOSAB Vol. 37,Issue 6,pp. 1838-1846(2020)→Simple and broad THz
- **THz pump spectroscopy E_{max}≈ 100 kV/cm |μJ pulse energy, nonlinear and collective behaviors induced by the intense THz fields** (JOSABVol. 25,Issue 7,pp. B6-B19(2008))
- **Manipulation and acceleration of charged particles E_{max}≈ 1 –100 MV/cm |(multi-)mJ pulse energy acceleration of proton & relativistic electron beams, X-ray free electron laser, etc.**

C) The method



B) The role of frequency of THz pulses



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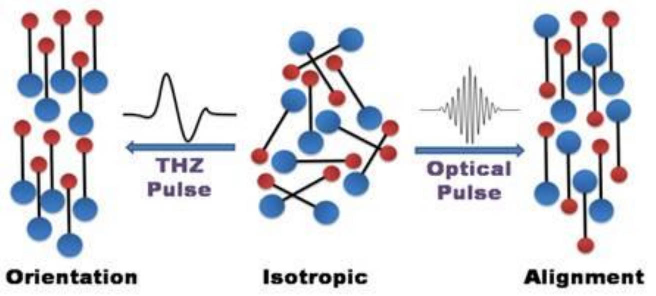
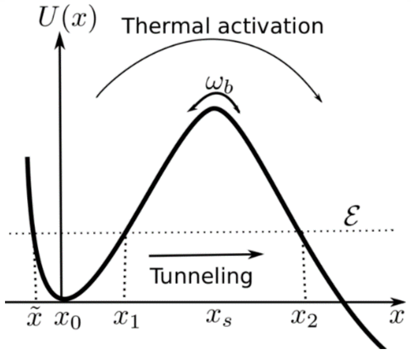
Terahertz reaction Control in Gas phase





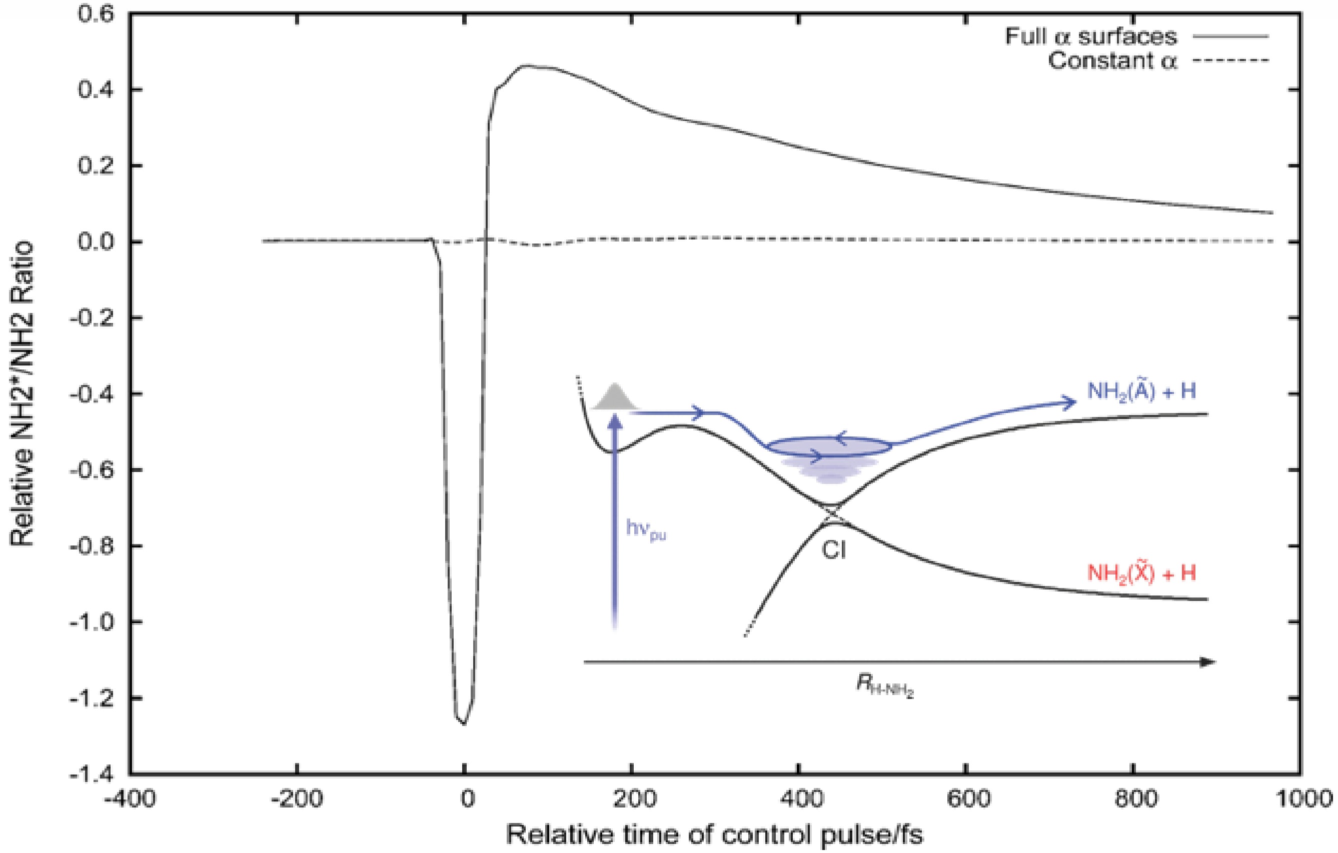
Objectives:

1. Terahertz alignment/rotational excitation of molecules prior dissociation with minimal ionization
2. Optical bias during fast (XUV) photodissociation→ Altering polarizabilities of excited states/influencing curve crossings
3. Modulating barrier height of tunneling processes of light fragments such as hydrogen (or electron)

What we will measure:

Energy disposal (electronic/rotational/vibrational populations), molecular alignment (terahertz/XUV pump probe absorption, fluorescence anisotropy), product yields

Example: Calculation of NH_2*/NH_2 branching ratio from the photodissociation of NH_3 under terahertz field



JPCA, 2012, 116, 11228

3 Effect of 150 fs wide, 0.7 eV non resonant control pulse applied at times before, during, and after application of a 50 fs wide, 4.7 eV excitation pulse, on the NH_2*/NH_2 branching ratio in the dissociation of ammonia. The ratio is relative to the natural branching ratio, i.e., that obtained with no control pulse. The solid line represents calculations done with all available dipole and polarizability surfaces, while the dashed line is the plot for calculations carried out using constant polarizability surfaces (11.8 and 13.5 au for the X- and A-states, respectively)

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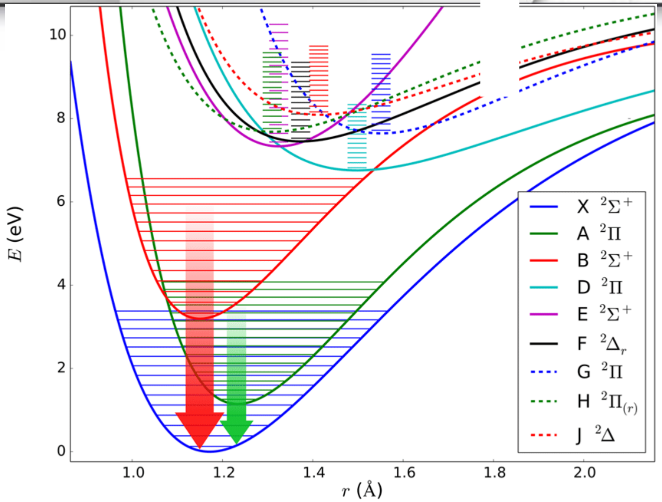
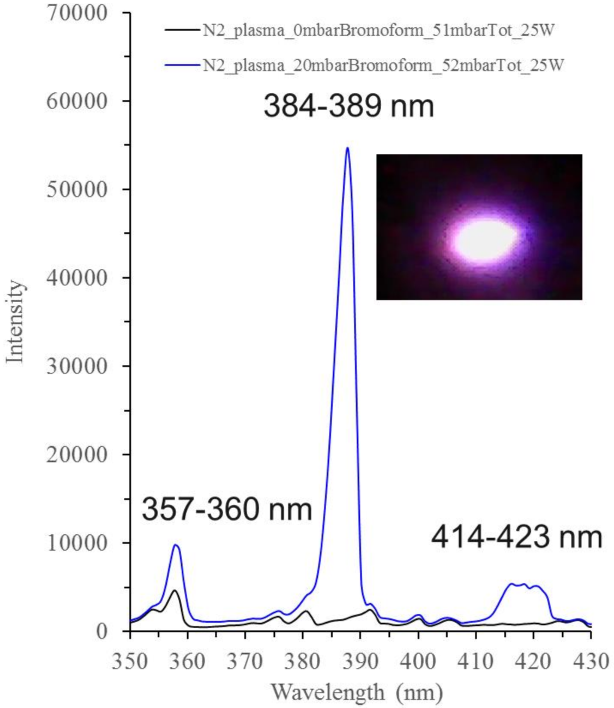
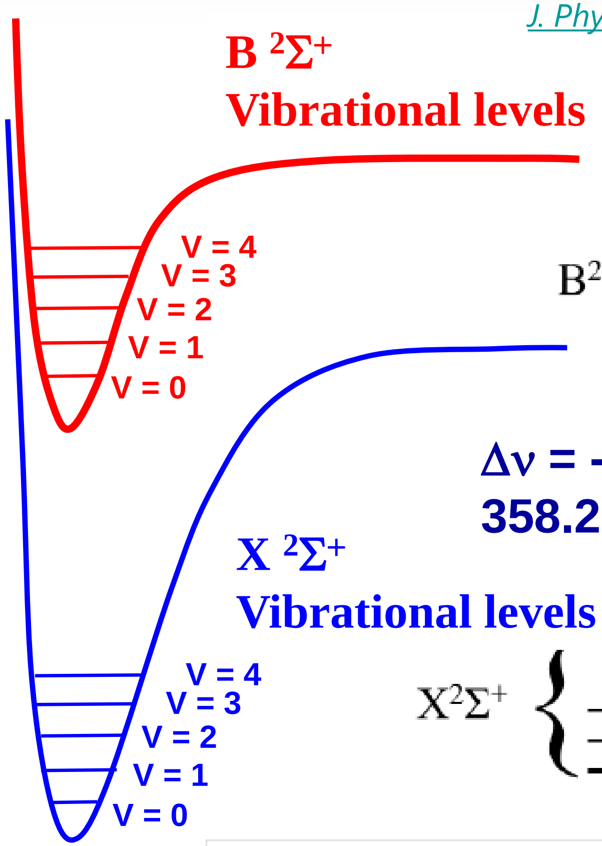
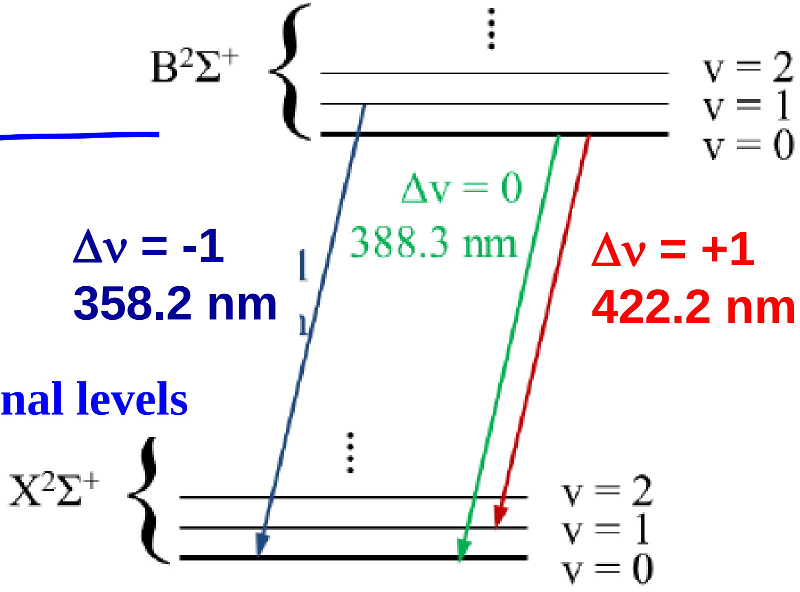
Vibrational and rotational energy levels of CN radical $B^2\Sigma^+ \rightarrow X^2\Sigma^+$ CN Violet System

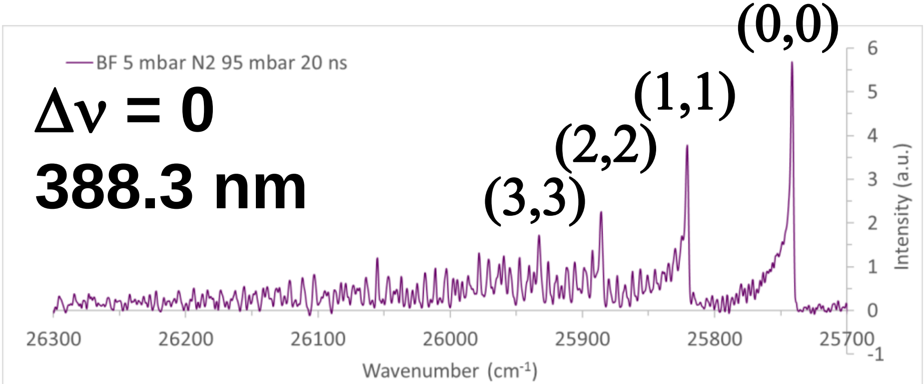


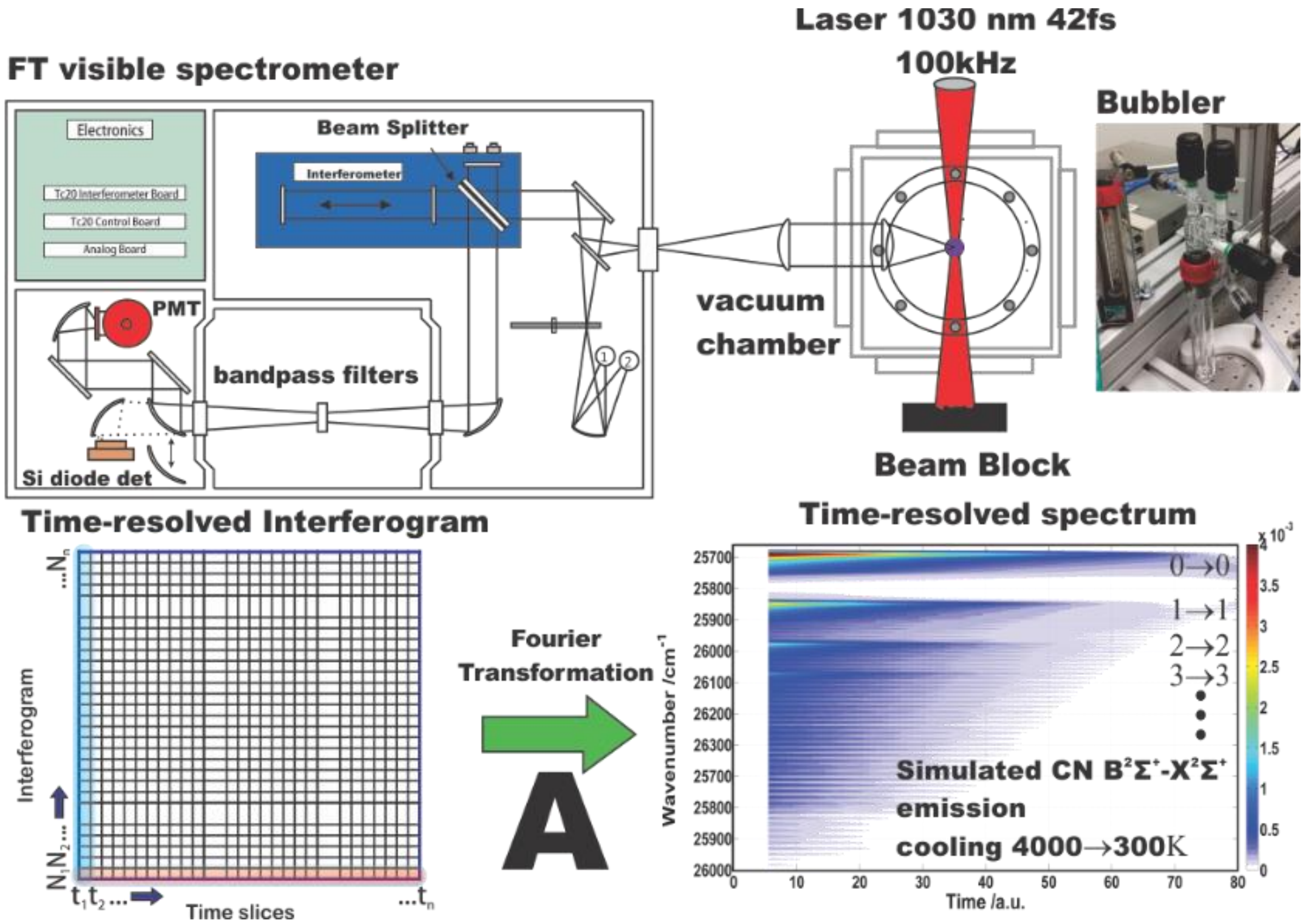


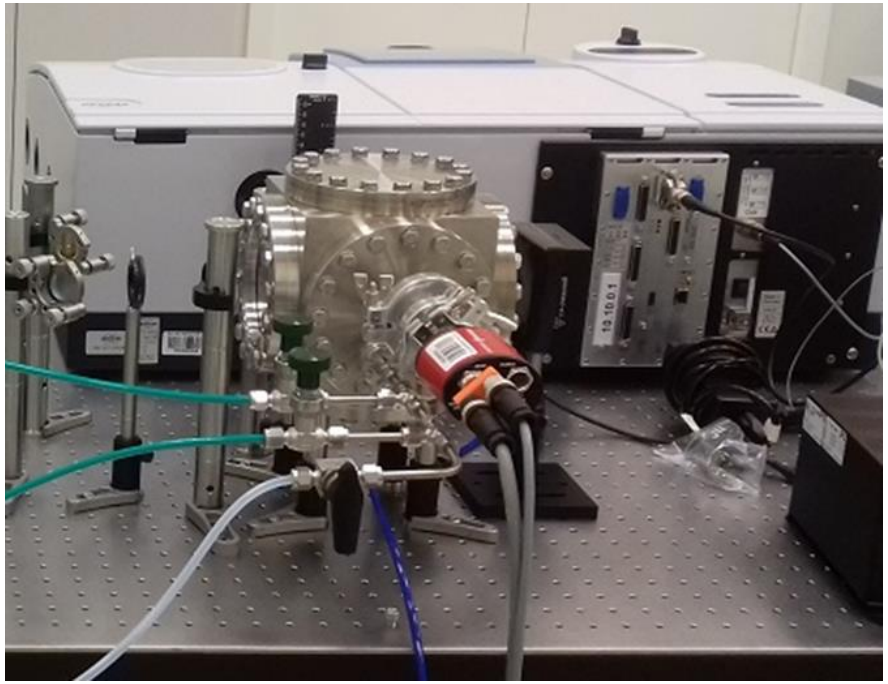


J. Phys. Chem. A 2020, 124, 14, 2755–2767






FT visible spectrometer
Electronics
Tc20 Interferometer Board
Tc20 Control Board
Analog Board
Beam Splitter
Interferometer
PMT
bandpass filters
Si diode det
Laser 1030 nm 42fs
100kHz
vacuum
chamber
Beam Block
Bubbler
Time-resolved Interferogram
Interferogram
Time slices
Fourier
Transformation
Time-resolved spectrum
Wavenumber /cm⁻¹
Time /a.u.
0→0
1→1
2→2
3→3
Simulated CN B²Σ⁺-X²Σ⁺
emission
cooling 4000→300K



Coulomb explosion of $CHBr_3$, CH_3CN,CH_3OH molecules

$$N_2 \rightarrow N^+ + e^- + N \tag{1}$$

$$e^- + N_2(X^1\Sigma_g^+) \rightarrow N_2^+(X^2\Sigma_g^+) + e^- + e^- \quad [15.5\ \text{eV}] \tag{2}$$

$$e^- + N_2(X^1\Sigma_g^+) \rightarrow N_2^+(B^2\Sigma_u^+) + e^- + e^- \quad [19\ \text{eV}] \tag{3}$$

$$e^- + N_2(X) \rightarrow 2N + e^- \tag{4}$$

$$C(^1D) + N_2 \rightarrow CN + N \tag{5}$$

$$C^+ + N_2 \rightarrow N^+ + CN \tag{6}$$

$$C_2 + N_2 \rightarrow 2CN \tag{7}$$

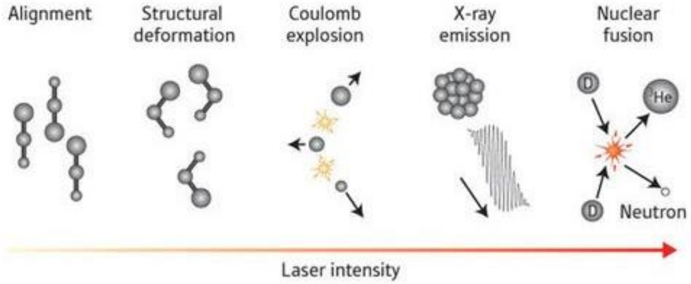
$$C_2 + N \rightarrow CN + C \tag{8}$$

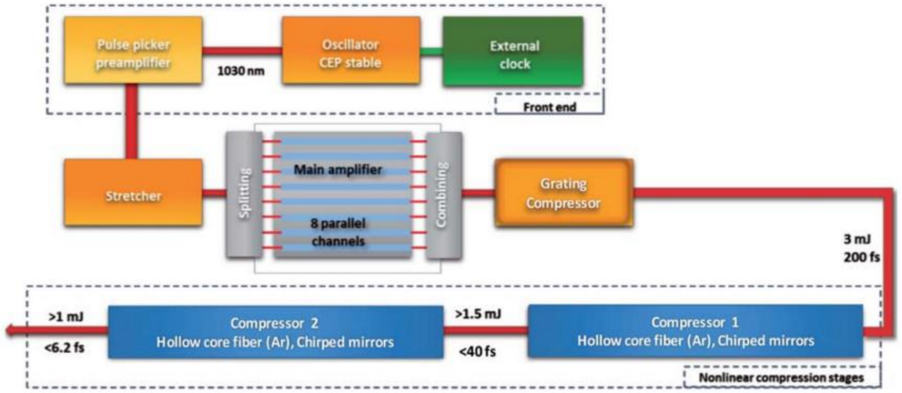
$$C_2 + 2N \rightarrow 2CN \tag{9}$$

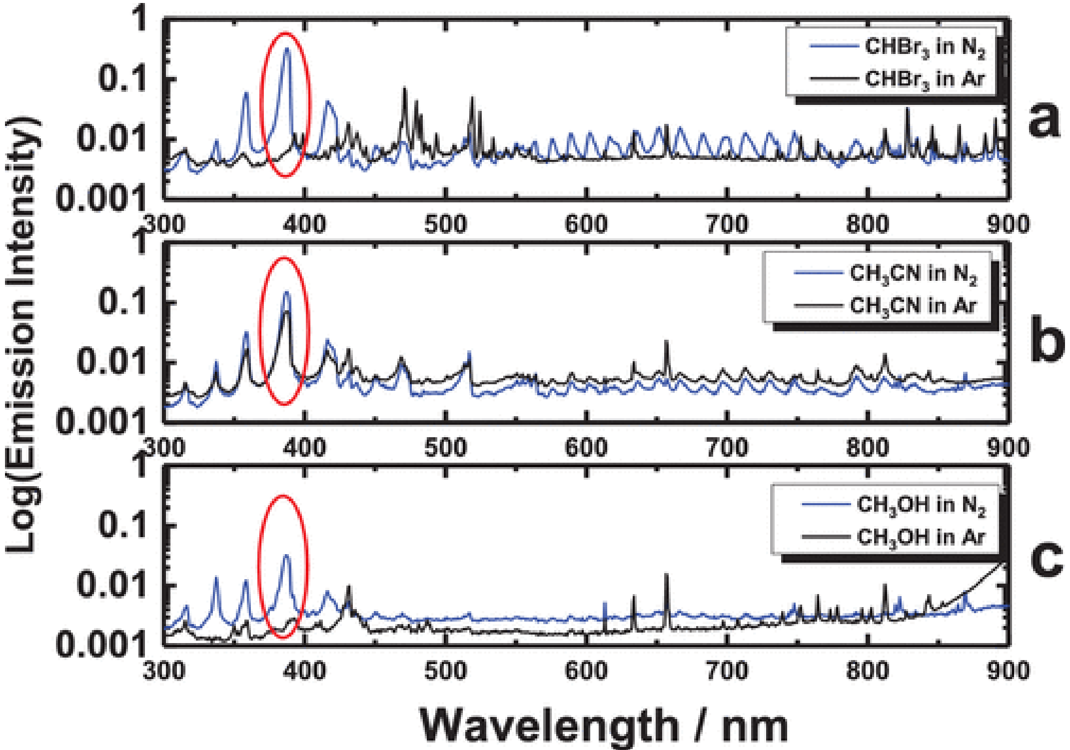
$$CH + N \rightarrow CN + H \tag{10}$$

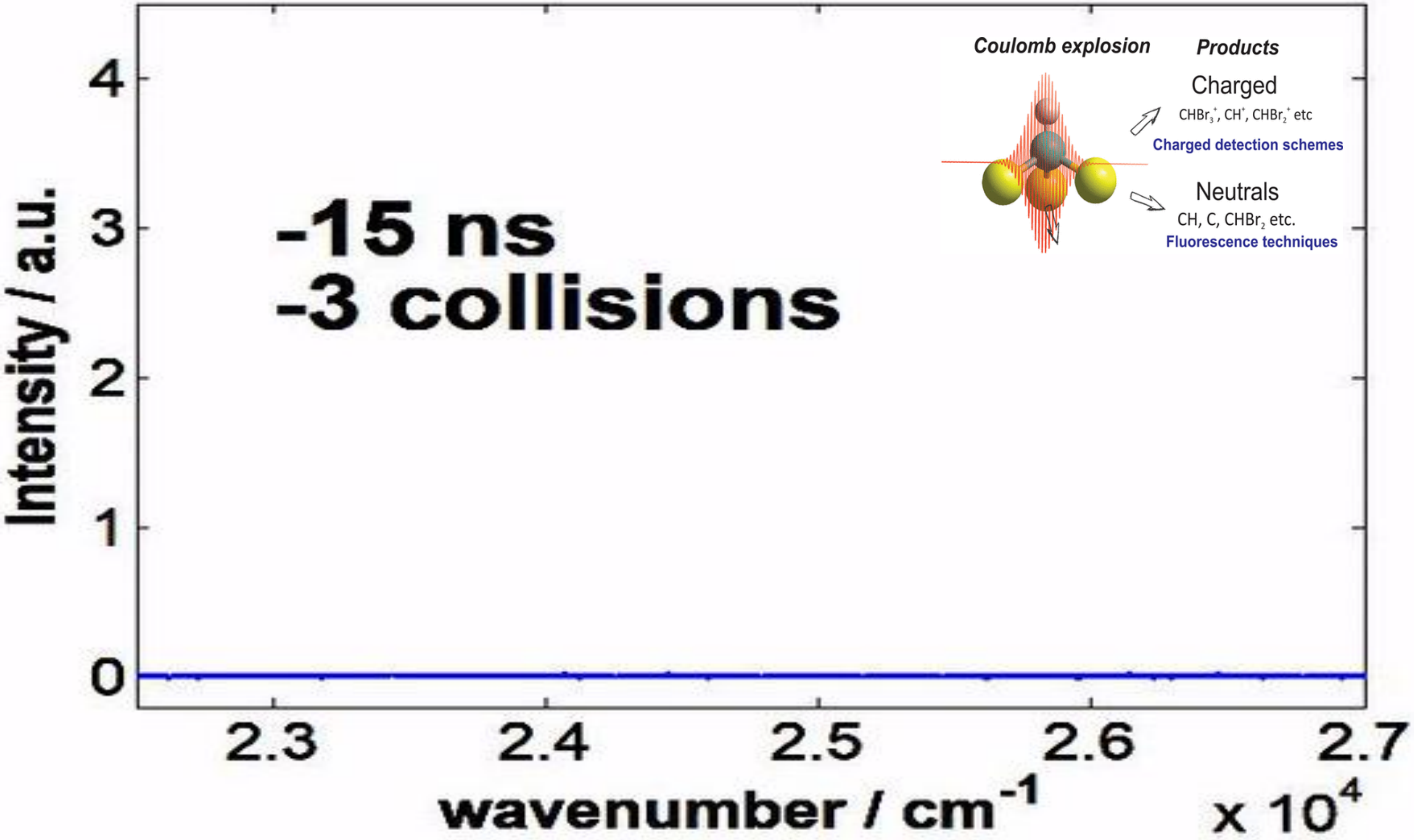
$$e^- + CN(X^2\Sigma^+) \rightarrow CN(B^2\Sigma^+) + e^- \tag{11}$$

$$N_2(B^3\Sigma_g) + CN(X^2\Sigma^+) \rightarrow CN(B^2\Sigma^+) + N_2(X^1\Sigma_g^+) \tag{12}$$



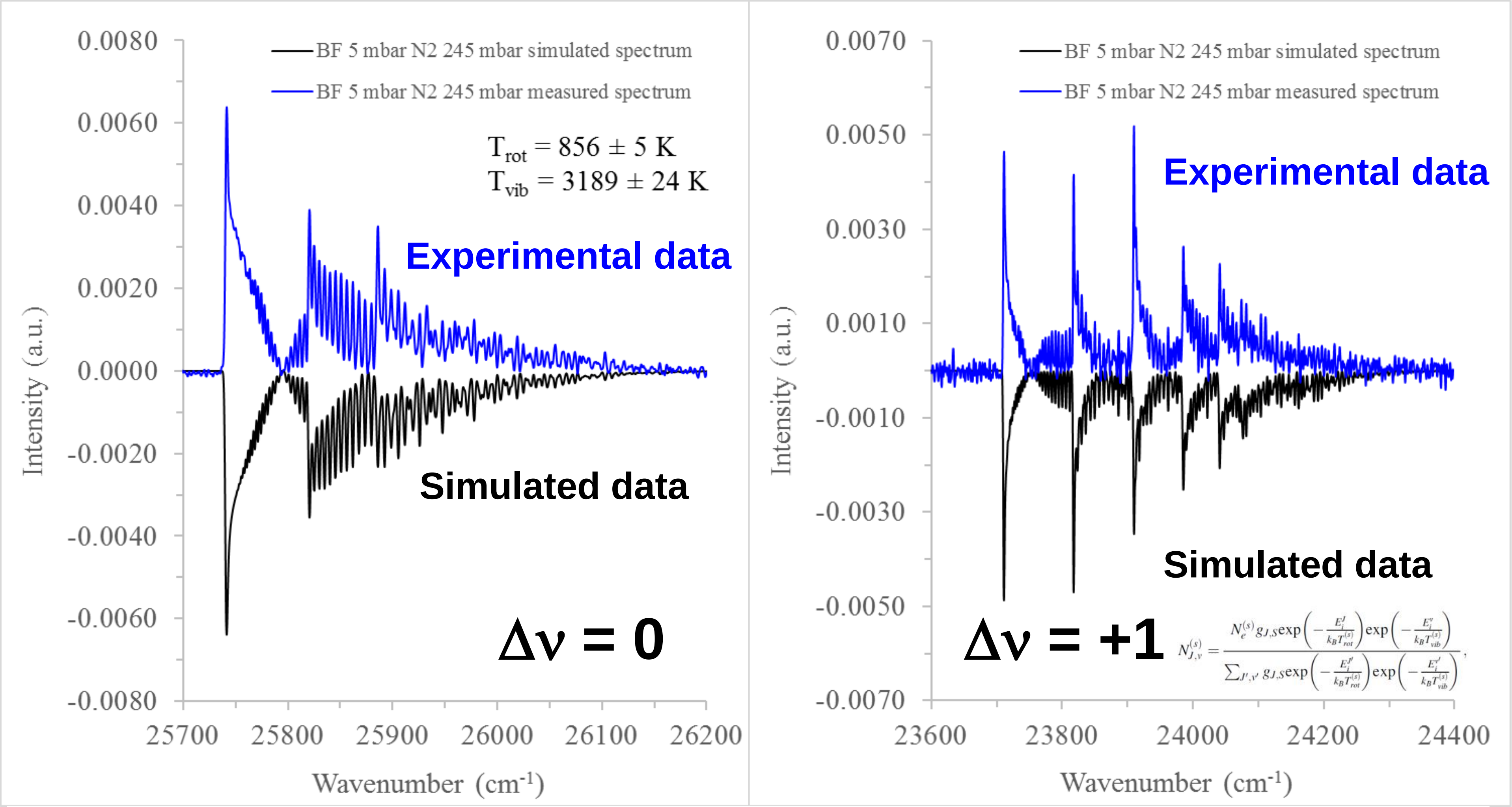






Coulomb explosion
Products
Charged
$CHBr_3^+$, CH^+, $CHBr_2^+$ etc
Charged detection schemes
Neutrals
CH, C, $CHBr_2$ etc.
Fluorescence techniques
-15 ns
-3 collisions
Intensity / a.u.
0
1
2
3
4
2.3
2.4
2.5
2.6
2.7
wavenumber / cm^{-1}
x 10^4

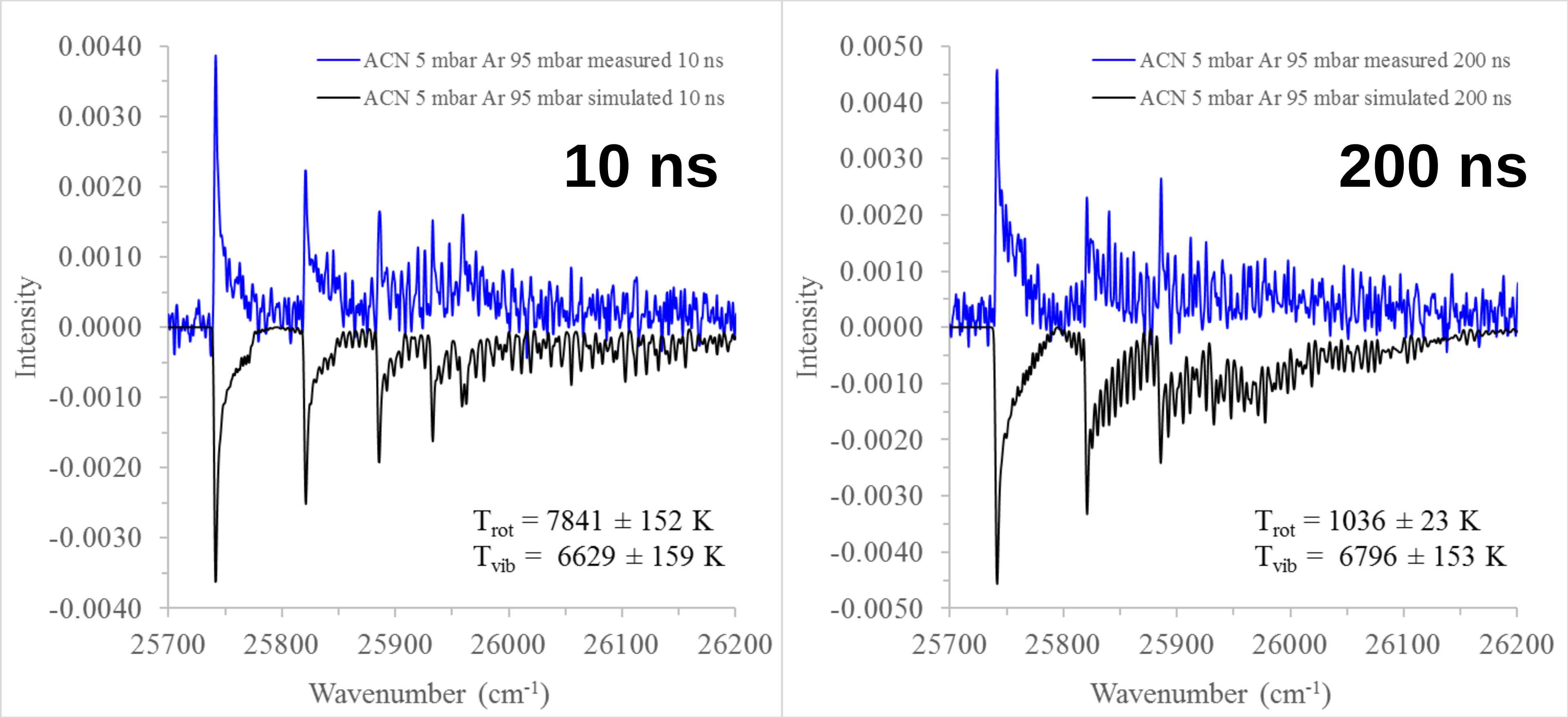
Spectral Fitting experimental data



$$N_{J,v}^{(s)} = \frac{N_e^{(s)} g_{J,s} \exp\left(-\frac{E_J'}{k_B T_{rot}^{(s)}}\right) \exp\left(-\frac{E_v'}{k_B T_{vib}^{(s)}}\right)}{\sum_{J',v'} g_{J,s} \exp\left(-\frac{E_J'}{k_B T_{rot}^{(s)}}\right) \exp\left(-\frac{E_v'}{k_B T_{vib}^{(s)}}\right)},$$

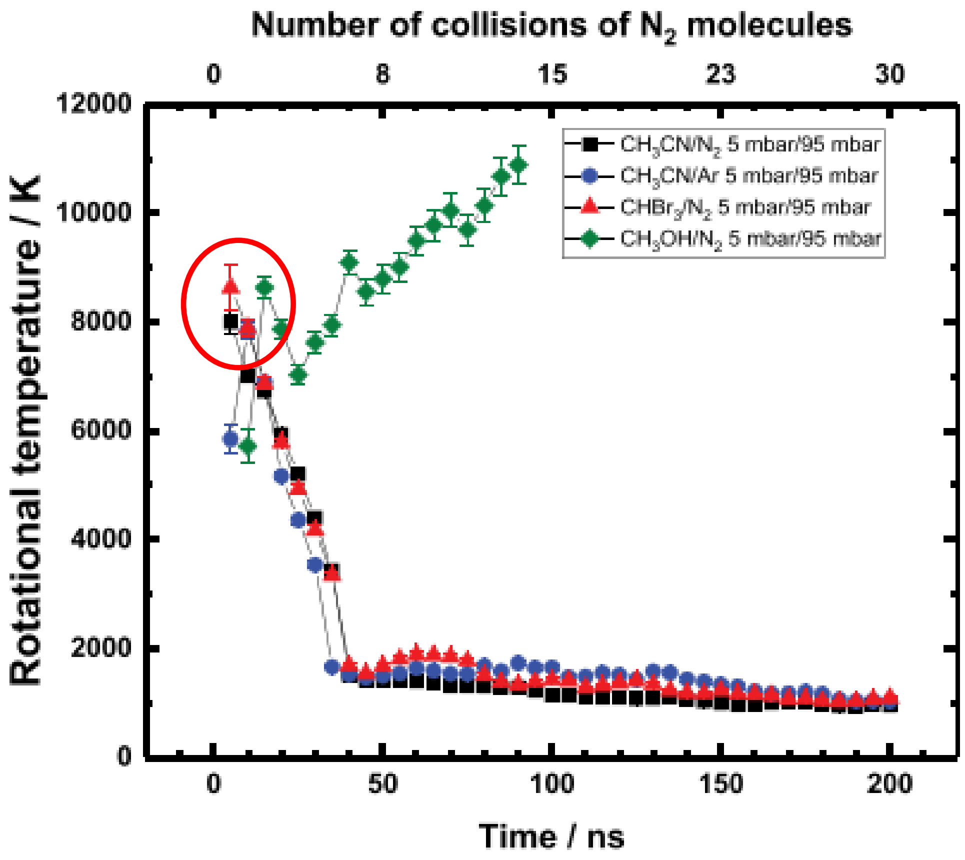
Non-equilibrium between the rotational and vibrational levels (modified Boltzmann distribution)

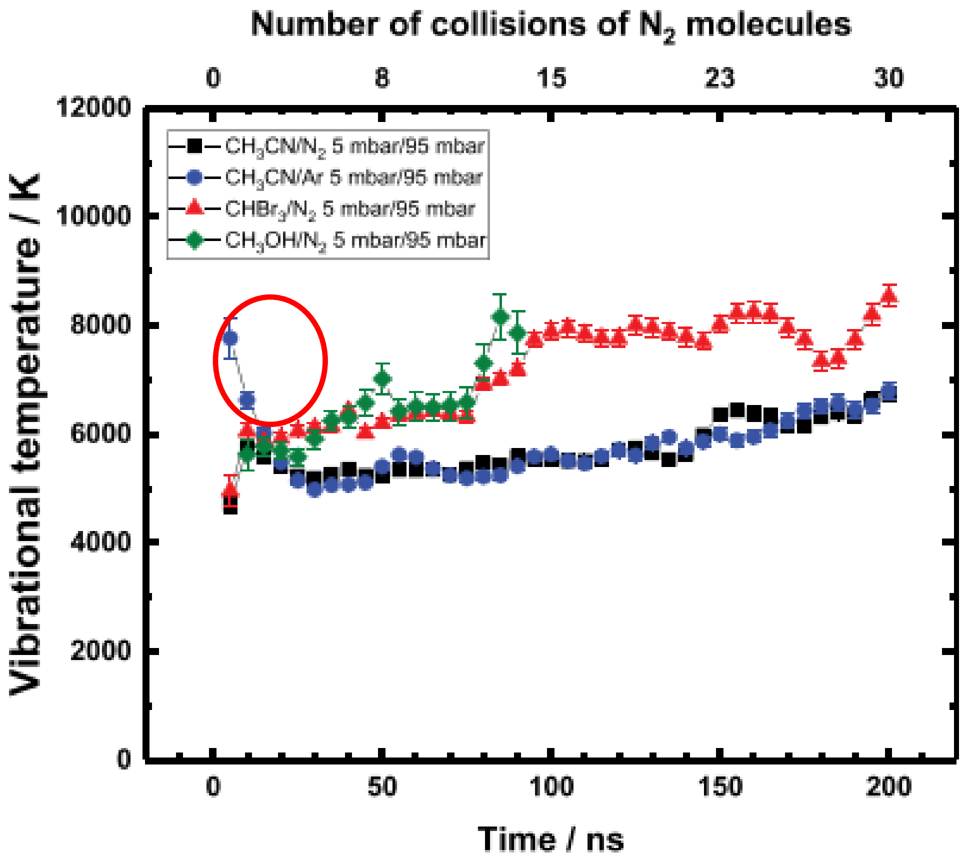
Time dependent spectral changes in CH_3CN/Ar samples (5 mbar/95 mbar)



Significant decrease in rotational temperature is observed within the first 200 ns: from ~7800 K to ~1000 K

CN radical Direct or Indirect production?





- CN is ‘hot’ from $CH_3CN \rightarrow$ direct production probable

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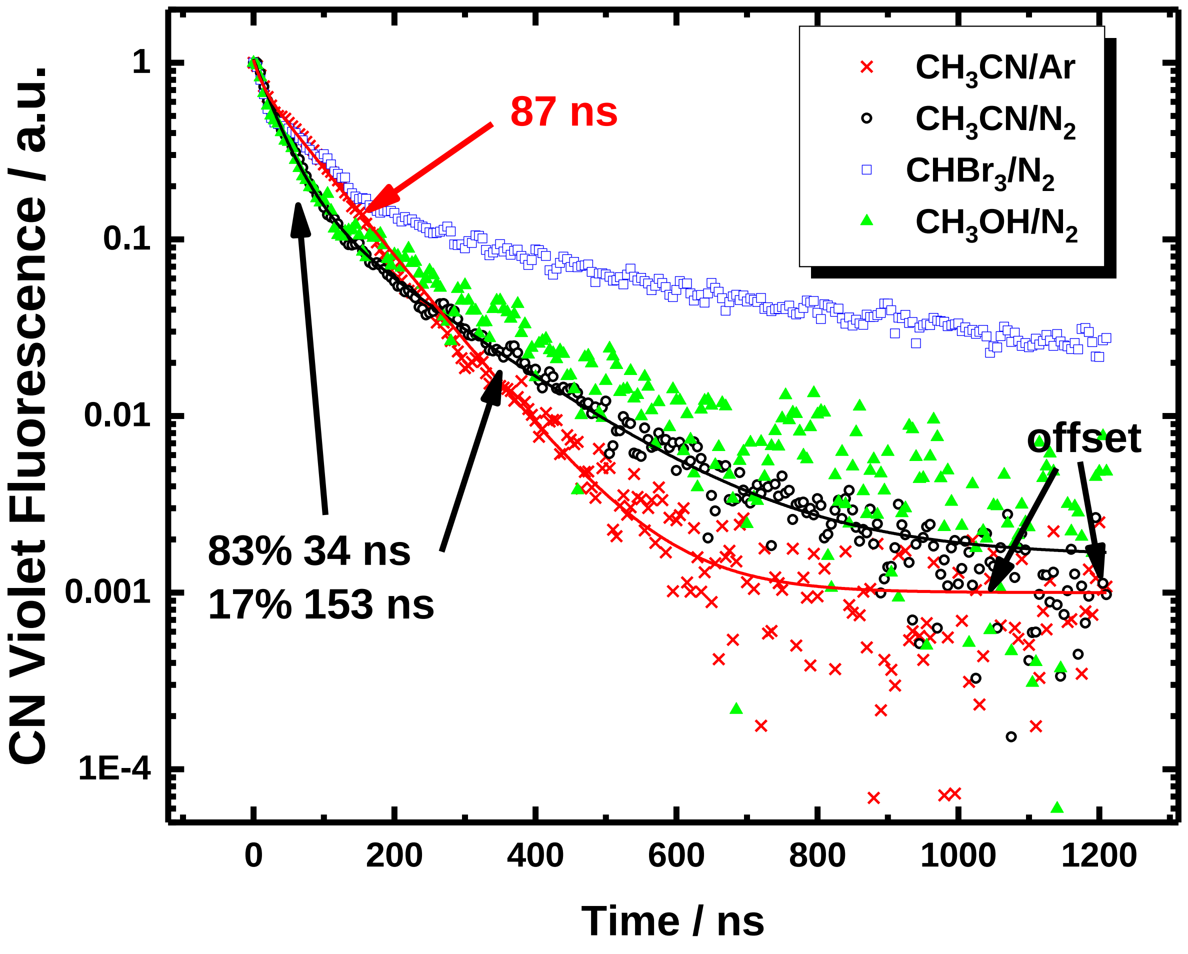
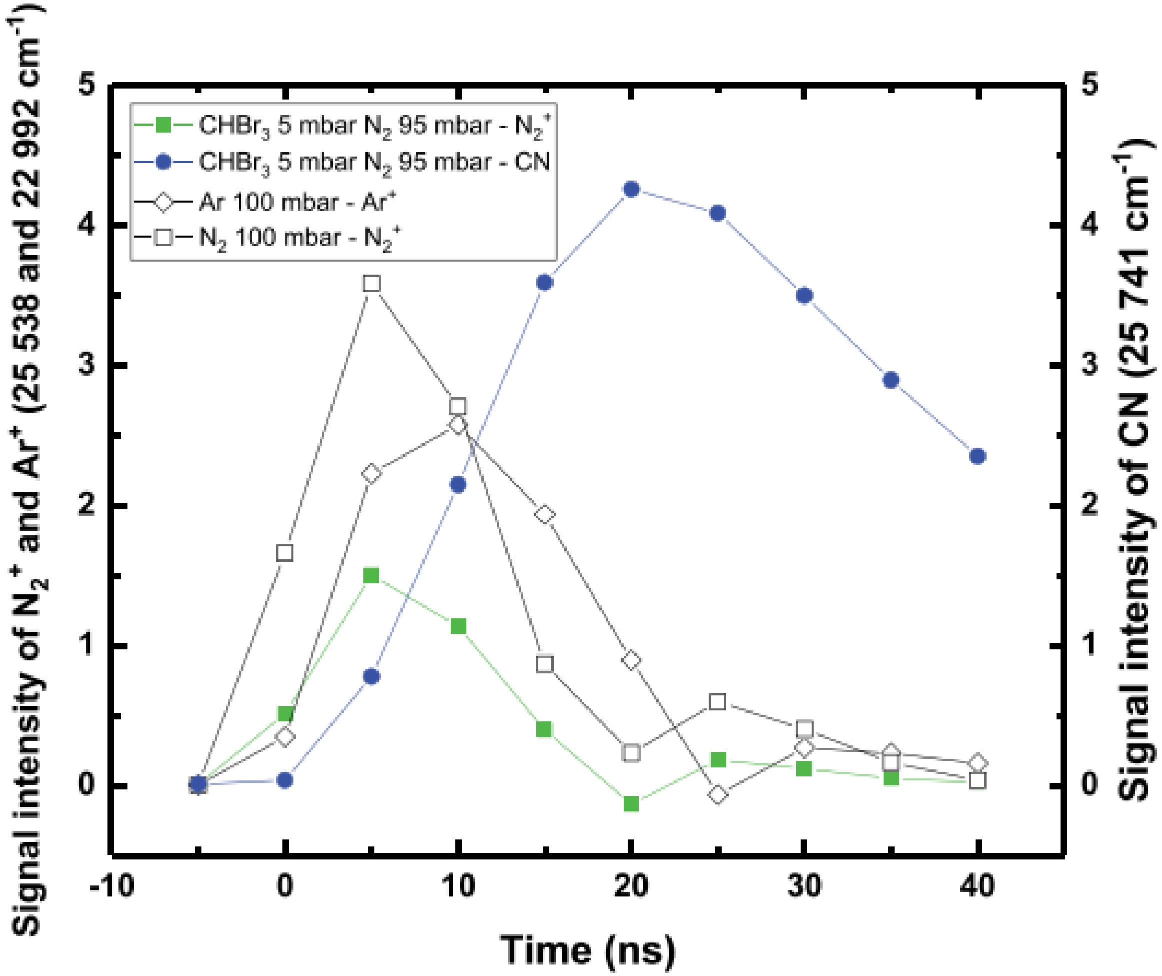
CN radical Direct or Indirect production?





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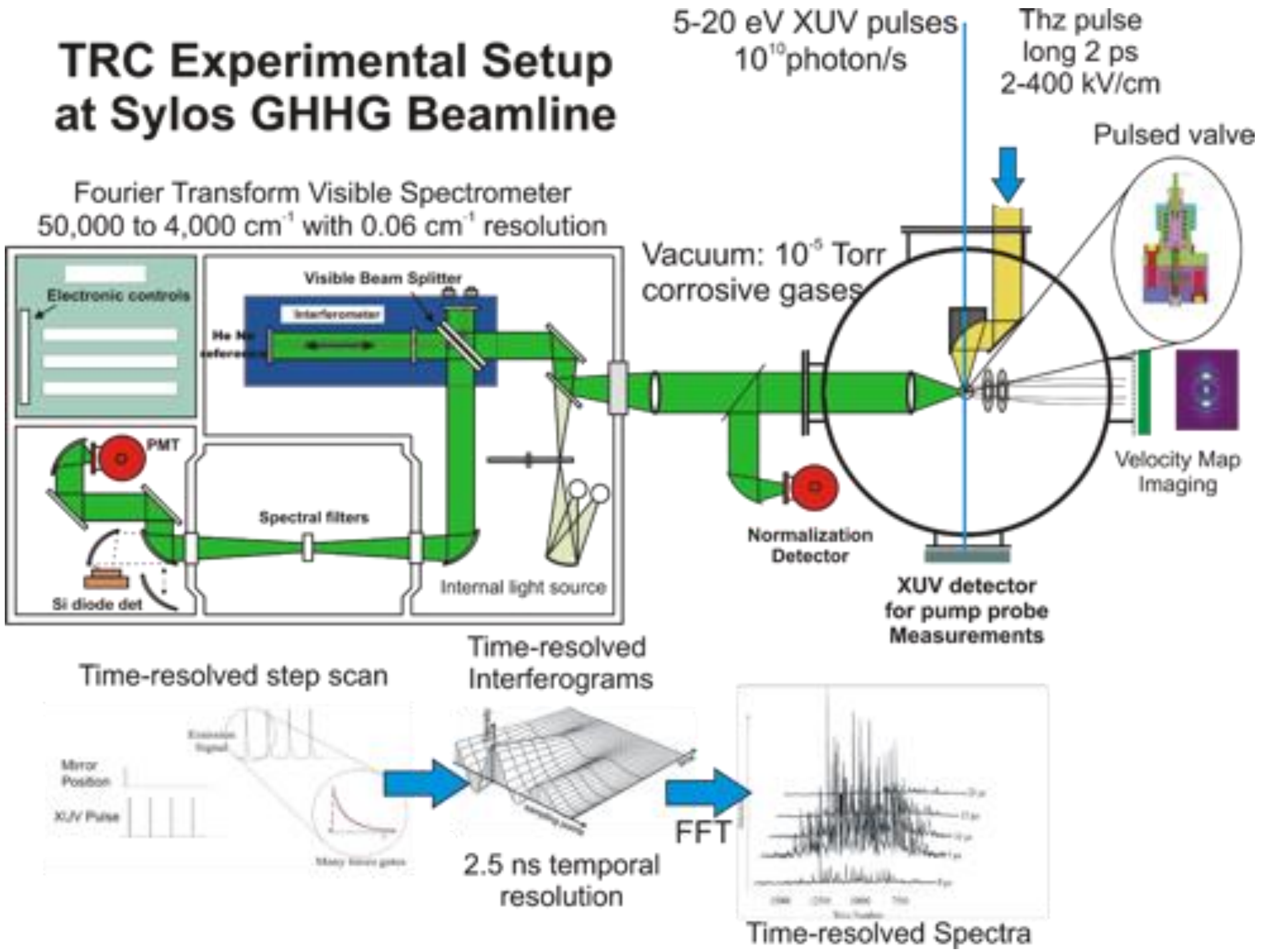
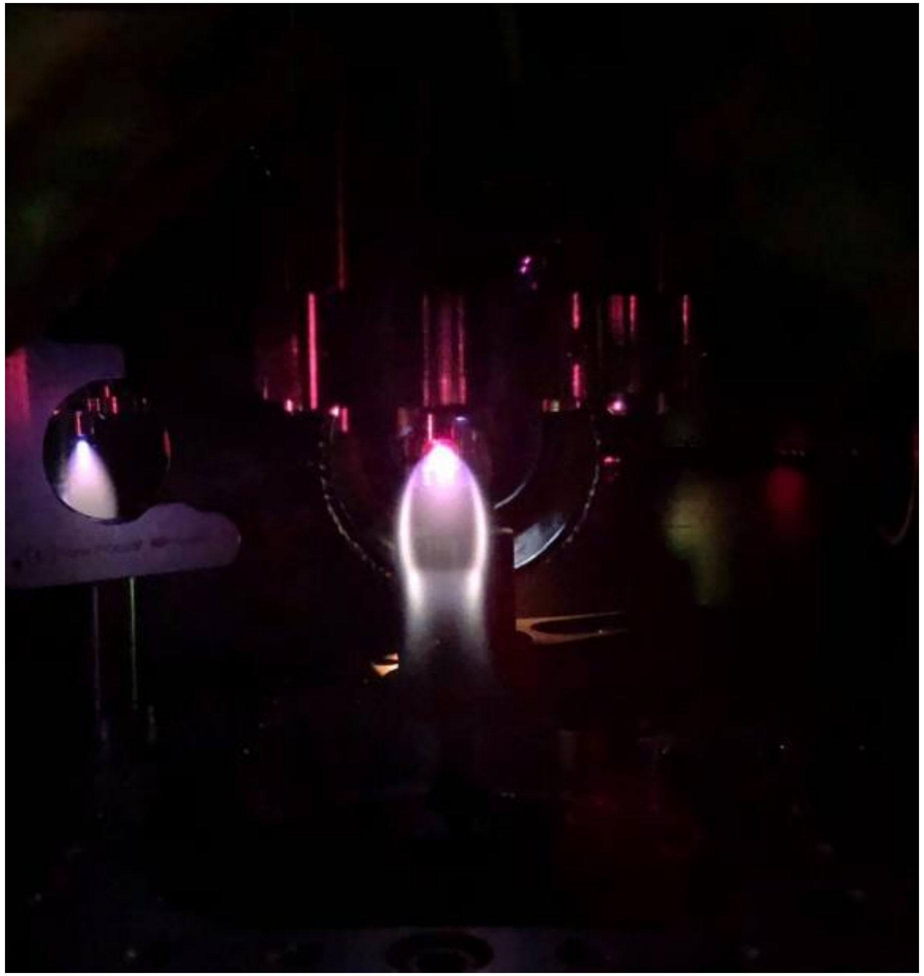
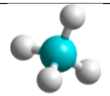
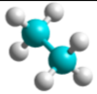
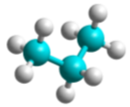
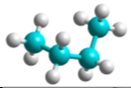
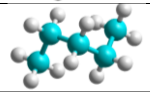
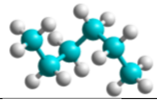
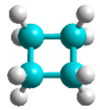
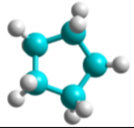
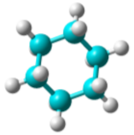
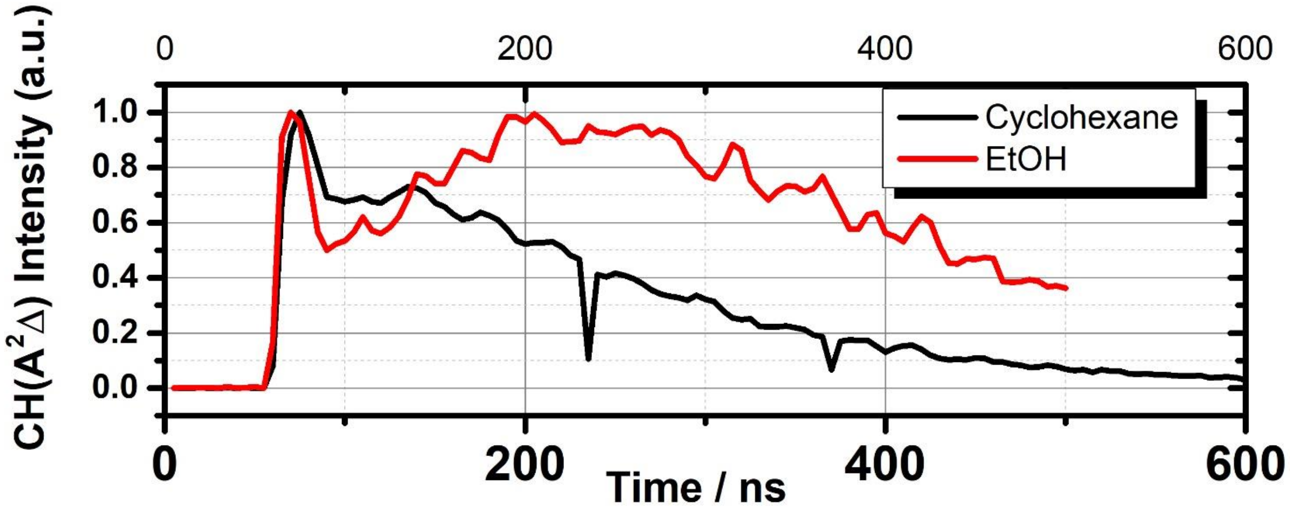
TRC Experimental Setup at Sylos GHHG Beamline

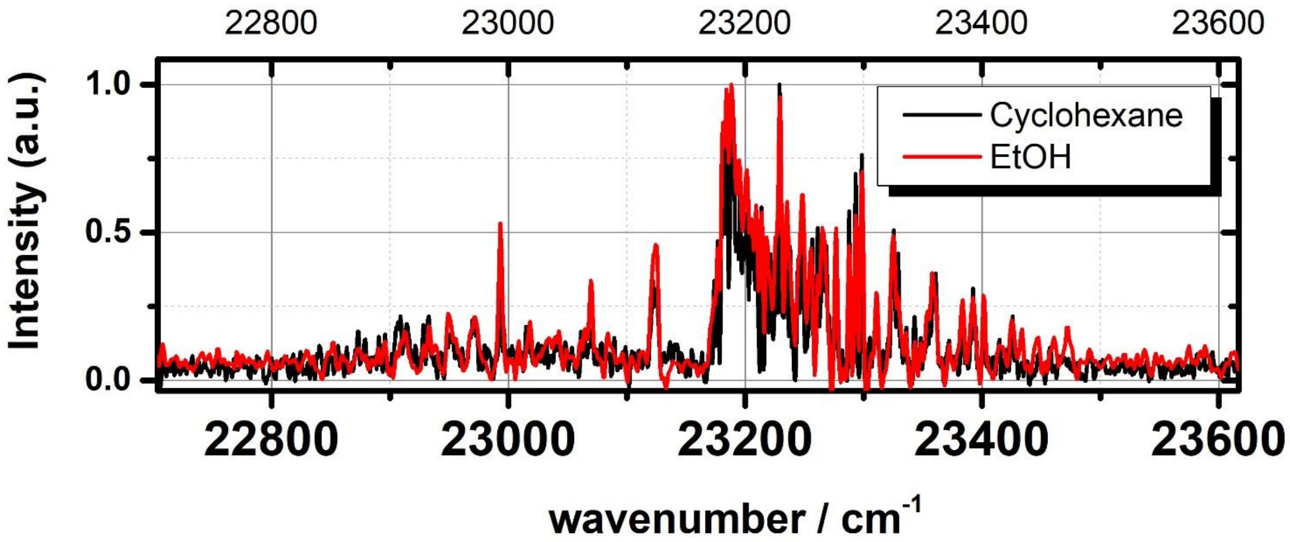




CH production in hydrocarbons

Name	formula	3d model	1^{st} ionization	Total# of electrons/number of nuclei	
methane	CH_4		12.61eV	16/5	3.2
ethane	C_2H_6		11.1eV	30/8	3.75
propane	C_3H_8		11.1eV	44/11	4
butane	C_4H_{10}		10.5eV	58/14	4.14
pentane	C_5H_{12}		10.37eV	72/17	4.23
hexane	C_6H_{14}		10.29eV	86/20	4.3
cyclobutane	C_4H_8		9.82eV	56/12	4.66
Cyclopentane	C_5H_{10}		9.83eV	70/15	4.66
cyclohexane	C_6H_{12}		9.8eV	84/18	4.66





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